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Chemical and Biological Characterization of Leachates from Coal Solid Wastes

Illinois State Geological Survey, Urbana

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Industrial Environmental Research Lab.
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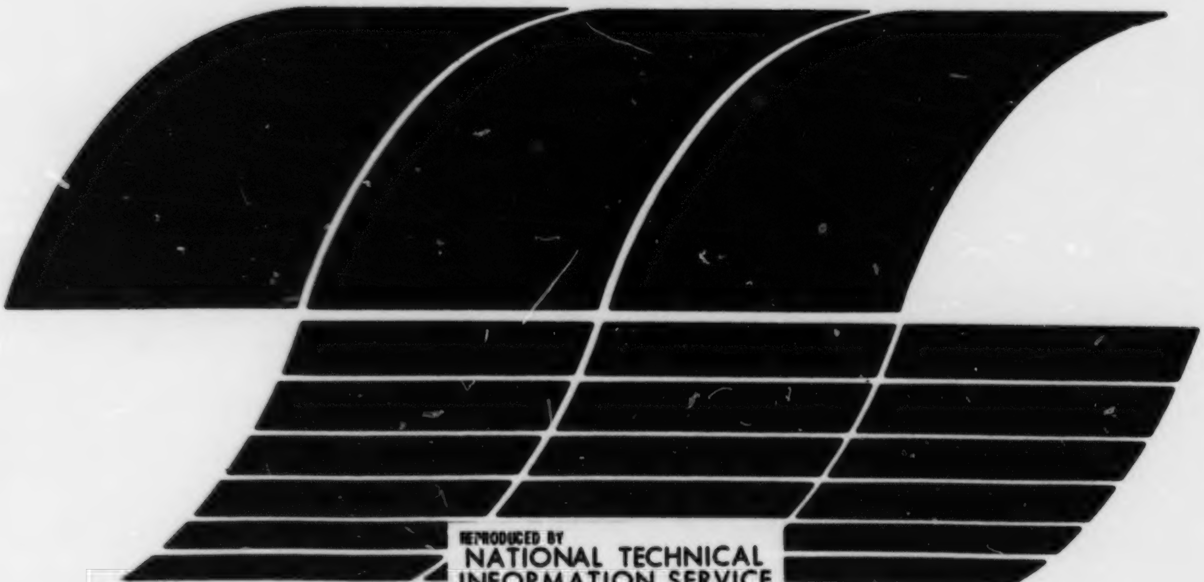

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March 1980

Chemical and Biological Characterization of Leachates from Coal Solid Wastes

by

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16. ABSTRACT

The report gives results of the chemical and mineralogical characterization of coal solid wastes. The wastes included three Lurgi gasification ashes, mineral residues from the SRC-I and H-Coal liquefaction processes, two chars, two coal-cleaning residues, and a fly-ash-and-water-quenched bottom ash (slag) from a coal-fired power plant. Leachates generated from the solid wastes at eight pH levels and under two different gas atmospheres were analyzed for more than 40 chemical constituents. Thermodynamic speciation of inorganic ions and complexes in solution were modeled. The modeling demonstrated that similar mineral phases controlled the aqueous solubility of the major ionic species for all wastes. Adsorption and coprecipitation of trace metals with iron, manganese, and aluminum oxides and hydroxides were thought to be the likely controls on trace metal concentrations in the leachates. A high degree of attenuation of the leachate constituents by soils was observed. Soil properties controlled the degree of attenuation to a greater extent than did the chemical concentrations of the leachates. Results of acute 96-hour static bioassays using fathead minnows identified mortality as being caused by the combined effect of pH and total ionic strength of the leachate.

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Wastes	Ashes	Stationary Sources		
Coal	Coal Gasification	Biological Properties	21D	13H
Combustion	Coal Preparation	Chars	21B	
Chemical Properties	Fly Ash	Coal Cleaning	07D	
Minerals	Slags		08G	11B
	Leaching			07A

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ABSTRACT

Eleven coal solid wastes were characterized chemically and mineralogically. The wastes comprised three Lurgi gasification ashes, mineral residues from the SRC-I and H-Coal liquefaction processes, two chars, two coal-cleaning residues, and a fly ash and water-quenched bottom ash (slag) from a coal-fired power plant. Leachates that were generated from the solid wastes at four pH levels and under two different gas atmospheres were analyzed for more than 40 chemical constituents. These leachates were also used in soil attenuation studies and in acute 96-hour static bioassays using fathead minnow fry.

Sixty constituents were determined in the solid wastes; the major ones among them were Al, Ca, Fe, K, Mg, Na, S, Si, and Ti. Concentrations of other constituents such as B, Ba, Ce, Cl, Cr, F, Mn, Sr, Zn, and Zr were generally between 100 and 1000 ppm, and significant quantities (<100 ppm) of trace metals were also present. Of the approximately 60 chemical constituents measured in the solid wastes, a range of 2 to 13 in the aqueous extracts generated in the laboratory from the individual wastes exceeded minimum standards of water quality recommended by the federal government.

The most significant mineral transformations that occurred during coal conversion processing were those of the iron-bearing minerals. For example, pyrite—the predominant iron-bearing mineral identified in the feed coals—was converted to pyrrhotite by processes that employed a reducing atmosphere, such as liquefaction and charring. Pyrite was converted to the oxides—hematite, magnetite, and goethite—by processes that used an oxidizing atmosphere, such as Lurgi gasification and power-plant combustion. Pyrite remained unaltered in the coal-cleaning refuse.

Thermodynamic speciation of inorganic ions and complexes in solution was modeled using the computer program WATEQF. One-hundred-fifteen aqueous species were considered in the model, and saturation data were computed for more than 100 minerals. The model demonstrated that similar mineral phases controlled the aqueous solubility of the major ionic species for all the wastes. Furthermore, adsorption and coprecipitation of trace metals with iron, manganese, and aluminum oxides and hydroxides were thought to be likely controls on trace metal concentrations in the leachates.

Study of the soil attenuation of soluble constituents leached from the coal solid wastes used the dispersed soil method with three Illinois soils of widely varying character. The results showed that chemical constituents were attenuated by the soils to a high degree. The soil properties controlled the degree of attenuation to a greater extent than the chemical composition of the waste leachates. Elution of Mg, and in some cases Mn, from the soils could present the greatest potential for contamination from land disposal.

The results of 96-hour static bioassays indicated that the water-soluble constituents in equilibrium with the wastes generally were not acutely toxic to fathead minnow fry at near neutral pH's (7.0-8.5); however, there was complete mortality in both the high- and low-pH leachates. Mortality was identified as being caused by the combined effects of pH and total ionic strength of the leachate. Complex chemical, mineralogical, biological, and soil attenuation factors must be integrated when assessing the environmental impact of land disposal of solid wastes from coal utilization processes.

This report was submitted in partial fulfillment of Contract no. 68-02-2130 to the University of Illinois, and was executed by the Illinois State Geological and Natural History Surveys under partial sponsorship of the U.S. Environmental Protection Agency (EPA). Work was completed in June 1979.

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SECTION 1

INTRODUCTION

Because of the oil and natural gas shortages in recent years, much has been written about finding alternate energy sources. Since coal is so abundant in the United States, it is an important energy alternative; however, many of our coal reserves cannot be directly processed for energy production if the government enforces strict compliance with the Clean Air Amendments of 1977. Technologies do exist, however (or at least are being developed), that produce clean fuel from coal by removing the environmentally hazardous materials from the coal, and/or by converting the coal into oil and gas products.

No less than 13 low/medium-BTU and nine high-BTU gasification systems are being considered for commercial and government agency support. An additional 19 major liquefaction processes are being considered for commercial development. In addition to the major coal conversion techniques, there are many other coal processing methods that clean the coal before it is used for energy production.

Although the quality of fuels produced by these techniques is improved, the accessory elements from the coal are concentrated in the waste streams from the process plant. These waste products need to be characterized before environmentally acceptable methods for their disposal can be developed. Emerson (1978), for example, itemized 15 waste streams from liquefaction processes. Included in this list were five solids: particulate coal, ash and slag residues, char, spent catalyst, and spent absorbents. These wastes are as different as the processes that produce them; their nature depends upon the variables of the conversion techniques. The nature of the wastes also strongly depends upon the feed coal—and coal itself can be highly variable within any particular seam.

Until recently, research has emphasized the characterization of airborne contaminants. Several investigators, however—including Cavanaugh and Thomas (1977); Spaite and Page (1978); Cavanaugh, Corbett, and Page (1977); and Somerville and Elder (1978)—have characterized the waste streams from low/medium-BTU gasifiers. Filby, Shah, and Sautter (1978) characterized the trace elements in solid wastes from the Solvent Refined Coal (SRC-I) liquefaction process. Sinor (1977) determined that the flow rate of Ni, As, Cd, and Pb from a Lurgi gasification plant may be as high as several pounds per hour. Because of the large quantities of raw materials consumed, large quantities of accessory elements may be discharged even though they may be present in the whole coal in low concentrations.

The estimated quantities of solid wastes produced from coal conversion vary widely, but all are high. Sather et al. (1975) estimated that a commercial coal gasification plant with a capacity of 250 million cubic feet of gas per day will use about 8 million tons of coal and generate about 2.3 million tons of ash and dry refuse per year. Other investigators (Seay et al., 1972; Asbury and Hoglund, 1974) have estimated that the amount of residue generated by a single gasification plant would occupy an area of 625 acre feet per year; in 20 years the residue would cover 1,250 acres to a depth of 10 feet. In another report, van Meter and Erickson (1975) estimated that 400,000 tons of slag or ash would be produced annually by a 250 million scfd gasification plant. These estimates, however, do not include the wastes generated from coal pretreatment processes. Jahnig (1975) calculated that 4,804 tons of refuse per day would result from the pretreatment of coal before its use in the Bi-Gas high-BTU gasification process.

Detailed characterization of the wastes produced from coal conversion and processing is justified because of the volume of wastes produced and their extreme variability. Characterization alone, however, is insufficient to determine acceptable disposal methods. The accessory and trace elements present may or may not be in a form that allows mobility; therefore, it is necessary to determine which elements can be leached from the wastes under which circumstances.

Sun et al. (1978) and Stone and Kahle (1977) have run leaching tests on wastes from fluidized-bed gasifiers, but most research has been done on wastes other than those from coal conversion processes. Wewerka et al. (1978) have done extensive leaching tests on bulk refuse samples from the Illinois Basin under a wide variety of testing conditions. Chu, Krenkel, and Ruane (1976), Theis (1975), and Natusch et al. (1977) tried to determine which constituents could be leached from fly ashes. The solubility of trace and other accessory elements in gasification ashes and slags is important, but has not yet been investigated thoroughly. Data on fly ashes and slags produced in coal-fired furnaces may not be pertinent because the gasification ashes and liquefaction residues are produced under different conditions—namely, at high temperatures and pressures, and usually in a reducing atmosphere rather than in an oxidizing one. Thus, significant alterations in the mineralogy and solubility of the accessory elements in ash can effect the potential of these elements as pollutants.

Severe contamination could also result from the disposal of refuse from coal that was cleaned before combustion or conversion. It is well known that when the pyritic minerals in this refuse are exposed to air and oxidizing conditions, iron sulfates and acids are produced (Singer and Stumm, 1969; Smith, Svanks, and Halko, 1969; Jones and Ruggeri, 1969). Garrels and Thompson (1960) concluded that the rate of oxidation was chiefly a function of oxidation-reduction potential (Eh), and was independent of total Fe content. Similarly, Bell and Escher (1969) found that the production of acidic iron salts from pyrite was an almost immediate response to the atmospheric gas composition in contact with the water. Reversing the gases from air to nitrogen caused the acid formation to decrease, and reversing the gases from nitrogen to air caused the acid formation to increase. There is also some evidence that oxidation of Fe (II) can be affected by the catalytic responses of trace constituents such as copper (Stauffer and Lovell, 1969).

These results have far-reaching implications for those proposals that recommend using alkaline gasification ashes to neutralize acid mine refuse, or those that recommend disposing of ash and refuse together as landfill in strip mines. Probably, accessory elements in the ash and refuse will be extracted by the acid solution; trace elements may actually catalyze the formation of additional acid.

Characterizing the solid wastes and determining the leachable constituents that may be generated are important first steps in determining the potential pollution hazards from the disposal of these wastes. Furthermore, it is necessary to determine the fate of the soluble constituents upon disposal and the effect of leachates that are generated from the wastes upon biota.

PURPOSE AND EXPERIMENTAL DESIGN

The purpose of this study was to investigate the potential pollution hazards of eleven selected coal solid wastes. This study is part of ongoing research by the Illinois State Geological Survey into the characterization of coal and coal residues (Ruch, Gluskoter, and Kennedy, 1971; Ruch, Gluskoter, and Shimp, 1973; Ruch, Gluskoter, and Shimp, 1974; Gluskoter, 1975; and Gluskoter et al., 1977). The eleven wastes chosen for this study included: three Lurgi gasification ashes from runs employing three different feed coals; two liquefaction residues—an SRC-I dry mineral residue and an H-Coal vacuum still bottom mineral residue; a high-sulfur and low-sulfur coal-cleaning refuse sample; a high- and low-temperature char; and a fly ash and bottom ash (slag) from a coal-fired power plant.

Listing detailed descriptions of all the available coal conversion and processing technologies is beyond the scope of this investigation; such descriptions are available elsewhere (Braunstein, Copenhaver, and Pfuderer, 1977; Parker and Dykstra, 1978). To understand the nature of the waste samples studied, however, we have included descriptions of the technologies used to produce these solid waste samples.

To determine the potential pollution hazards of the solid wastes, the study was divided into six stages:

1. Mineralogical characterization of the feed coals and the solid wastes.
2. Chemical characterization of the solid residues.
3. Determination of the soluble constituents of the wastes.
4. Application of equilibrium solubility models to determine mineral phases controlling the aqueous solubility of the major ionic species.
5. Identification of the interactions between earth materials and leachates generated from the wastes, as would occur in a disposal environment.
6. Determination of the acute toxicity of the generated leachates by conducting 96-hour static bioassays using fathead minnow fry.

SECTION 2

CONCLUSIONS

1. Chemical and mineralogical characterization of solid wastes from coal utilization processes showed that they had a wide range of chemical and mineral composition.

2. Characteristics of the feed coal and process operating variables affected the mineral transformations that occurred during processing and the character of the solid wastes generated by a given process.

3. Thermochemical solubility modeling demonstrated that similar mineral phases controlled the aqueous solubility of many major, minor, and trace ionic species for all of the solid wastes.

4. Many metastable mineral phases—such as iron, aluminum, manganese, and silicon oxides and hydroxides—must be considered when predicting environmental impact during the initial leaching of coal solid wastes. Trace metal adsorption on or coprecipitation with these oxides and hydroxides is a probable control on the trace metal concentrations in coal-waste leachates.

5. The chemical constituents in the leachates were highly attenuated by all the soils, and the soil properties, rather than the chemical composition of the leachates, dominated the degree of attenuation. Elution of Mg, and in some cases Mn, from the soils could have the greatest potential for contaminating waters as a result of land disposal of coal solid wastes.

6. Approximately one-half of the leachates generated from the eleven coal solid wastes at their natural pH levels were acutely toxic to young fathead minnow fry.

7. Several acidified leachates were very toxic (LC-50 <1.0 mL/100 mL) and required large amounts of dilution (>1:100) to ensure survival of the minnows during 96-hour bioassay.

8. The acute toxicity of leachates equilibrated under anaerobic conditions did not significantly differ from the acute toxicity of similar leachates equilibrated under aerobic conditions.

9. The degree of a leachate's toxicity and the amount of dilution necessary to ensure survival of the minnows during a 96-hour bioassay was largely a function of the pH and total ion concentration of the leachate.

10. Some of the leacheates contained concentrations of Al, B, Ca, Cd, Cu, Fe, K, Li, Mn, Ni, Pb, SO_4, Sb, and Zn that may be hazardous to biota.

11. The SRC liquefaction residue, along with the fly ash and slag, for which the natural pH leachates were acidic, produced the leachates most toxic to fathead minnow fry in this study.

12. Complex chemical, mineralogical, biological, and soil attenuation factors must be integrated on a case-by-case basis to correctly assess the environmental impact of land disposal of solid wastes from a given coal utilization process.

SECTION 3

RECOMMENDATIONS

The potential environmental and economic consequences caused by the disposal of the solid wastes generated by even one large-scale coal utilization facility are impressive because of the sheer magnitude of the wastes generated. The major solid wastes are the refuse from coal cleaning; the ashes, slags, and chars from conversion processes; and the sludges from stack scrubbing and water cleanup. Clearly, careful planning is needed to mitigate adverse effects on the environment; however, planning can be effective only when there is an adequate data base.

The data base should contain information on the qualitative and quantitative characterization (both chemical and biological) of coal solid wastes. This information should include:

1. Quantitative determination of the accessory elements contained in the wastes
2. Determination of the solubility of the accessory elements under a variety of environmental conditions
3. Establishment of the effects of coal characteristics and process operating variables on the character of the solid wastes generated by a given process
4. Determination of methods for recovering economically valuable metals from the solid wastes
5. Determination of the ultimate fate of waterborne pollutants resulting from solid-waste materials
6. Characterization and quantification of both the acute and chronic biological toxicity and public health hazard associated with pollutants from coal solid wastes

Research should be conducted to improve and validate environmental goals, such as the Multimedia Environmental Goals (Cleland and Kingsbury, 1977). The goals should be aimed at protecting the integrity of the environment within realistic bounds.

The energy demands of the nation necessitate the large-scale construction of coal gasification, liquefaction, and scrubber plants. The conversion process designs are at the pilot and demonstration plant stages of development; more plants will undoubtedly be built within the next decade. On a scale this large, there are few precedents that could be used to predict the environmental impact of the disposal of waste products.

Through proper planning, valuable trace elements can probably be recovered from many wastes. We need basic and applied research to formulate those strategies and disposal options necessary to avoid the serious problems that could appear suddenly in large-scale operations. Furthermore, the research must be begun soon so that the data will be available for the planning of the initial large-scale coal conversion facilities.

SECTION 4

SOLID WASTES FROM COAL CONVERSION AND UTILIZATION

Descriptions of the more than 40 coal conversion technologies being studied for possible commercial development are contained in various technical literature; however, this study only contains descriptions of the Lurgi gasification and H-Coal and SRC-I liquefaction processes.

Both types of conversion processes—liquefaction and gasification—are meant to increase the hydrogen-to-carbon ratio of the coal and remove environmentally hazardous materials from the feed coals. Natural gas is composed of 75 percent carbon and 25 percent hydrogen by weight, with traces of environmentally unacceptable constituents (Linden et al., 1976). On the other hand, petroleum is 83 to 87 percent carbon, 11 to 15 percent hydrogen, and up to 4 percent oxygen, nitrogen, and/or sulfur (Ellison, 1967). Clean coal is approximately 75 percent carbon, only 5 percent hydrogen, and 20 percent additional constituents, including pyrite and organic sulfur (Linden et al., 1976). Thus, it is necessary to either increase the amount of hydrogen or decrease the relative quantity of carbon if coal is to be converted to a product containing useful quantities of oil or gas.

LURGI GASIFICATION

There are two classifications of gasifiers, low/medium-BTU and high-BTU. In order to synthesize gas from coal, three ingredients are needed: carbon, hydrogen, and oxygen (Braunstein, Copenhaver, and Pfuderer, 1977). Coal and steam provide the carbon and hydrogen respectively. In low-BTU processes, air is the combustant, and the raw gas has a heating value of 150 to 300 BTU/scf. For medium-BTU gasifiers, pure oxygen produces a raw gas with a heating value of 300 to 400 BTU/scf. Most low- and medium-BTU gasifiers can be upgraded to a high-BTU system (900 to 1,000 BTU/scf) by addition of a methanation step. The latter process produces a gas of pipeline quality that can fill commercial and residential needs. The low- and medium-BTU gasifiers are now primarily used on site for industrial purposes. Gasifiers can be further subdivided by the type of reaction bed used: fixed, fluidized, and entrained beds. Braunstein, Copenhaver, and Pfuderer (1977) give a detailed discussion of the reactor types.

The Lurgi gasification process has been commercially available since 1936 (Cavanaugh, Corbett, and Page, 1977); currently, 60 commercial plants use this process. The Lurgi is a fixed-bed, pressurized gasifier that operates with either air or oxygen and steam. Figure 1 shows a process schematic, and a material balance for gas production is given in Table 1. With the

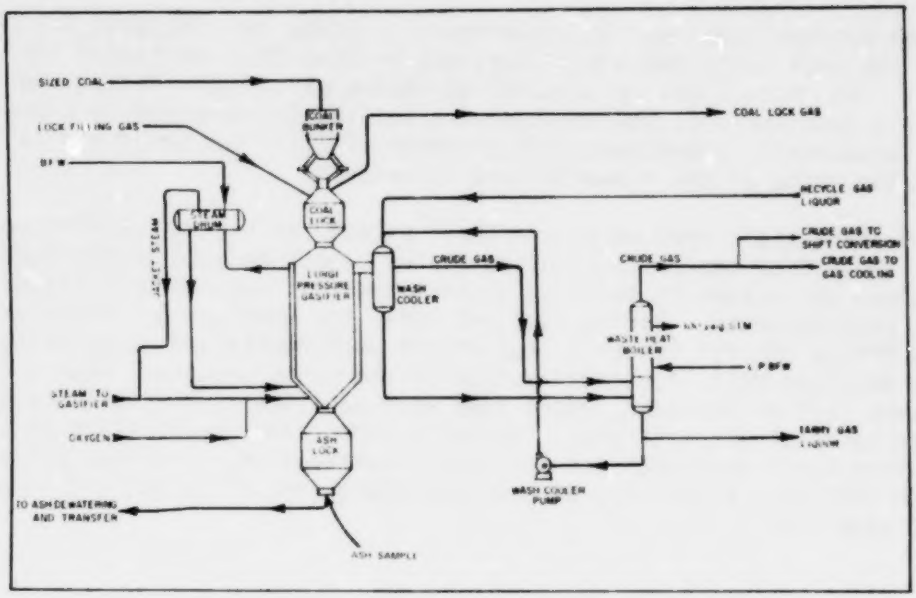
SIZED COAL
COAL BUNKER
LOCK FILLING GAS
BFW
COAL LOCK GAS
STEAM DRUM
JACKET STEAM
COAL LOCK
RECYCLE GAS LIQUOR
CRUDE GAS TO SHIFT CONVERSION
CRUDE GAS
CRUDE GAS
CRUDE GAS TO GAS COOLING
LURGI PRESSURE GASIFIER
WASH COOLER
WASTE HEAT BOILER
L P BFW
STEAM TO GASIFIER
OXYGEN
ASH LOCK
TARRY GAS LIQUOR
WASH COOLER PUMP
TO ASH DEWATERING AND TRANSFER
ASH SAMPLE

Figure 1. Flow scheme for gas production from the Lurgi process (Sinor, 1977).

TABLE 1. MATERIAL BALANCE FOR GAS PRODUCTION FROM THE LURGI PROCESS (SINOR, 1977)

Stream number component	4.1 lbs/hr	4.2 lbs/hr	4.3 lbs/hr	4.4 lbs/hr	4.5 lbs/hr	4.6 lbs/hr	4.7 lbs/hr	4.8 lbs/hr
CO_2						1,333,502	729,157	604,345
H_2S						13,538	7,403	6,135
C_2H_4						12,273	6,710	5,563
CO						611,677	334,464	227,213
H_2						84,859	46,401	38,458
CH_4						193,007	105,537	87,470
C_2H_6						19,730	10,788	8,942
N_2 + Ar			10,275			11,861	6,485	5,376
O_2			460,365			—	—	—
Total dry gas			470,640			2,280,447	1,246,945	1,033,502
Water	314,950	1,783,540			++	1,394,960	762,764	632,196
Coal (MAF)	1,250,300			19,639		—	—	—
Ash	373,220			373,220		—	—	—
Naptha						20,005	10,939	9,006
Tar oil					11,993	28,007	15,314	12,693
Tar					65,811	6,630	3,999	3,315
Crude phenols					173	8,272	4,991	4,136
NH_3						15,978	9,640	7,989
TOTAL	1,938,480	1,783,540	470,640	392,859	77,977	3,757,489	2,054,592	1,702,897

fixed-bed process, the coal is supported on a grate and the gases are passed through the coal, with the hot product gas exiting from the top of the reactor. The product gas is scrubbed to remove particulate matter and is eventually desulfurized, and the hydrogen sulfide is converted to elemental sulfur (Braunstein, Copenhaver, and Pfuderer, 1977). The solid ash falls through the grate of the fixed bed and is removed.

Noncaking coals need no pretreatment except for sizing. Caking coals such as those from the eastern United States cannot be used in the Lurgi process unless the system is modified so that the coal bed can be agitated to prevent agglomeration. During 1973 and 1974, the American Gas Association and the Office of Coal Research studied the performance and suitability of various American coals for gasification by the Lurgi process. Four different coals were sent to Scotland, where they were gasified in the full-scale modified gasifier at Westfield. The solid ashes from gasification of three of the feed coals were analyzed for this investigation. The feed coals included Illinois Herrin (No. 6) and Harrisburg (No. 5) Coals, and a Montana Rosebud seam coal.

LIQUEFACTION: H-COAL AND SRC-I

Coal conversion technologies termed liquefaction can produce not only a liquid fuel but also gaseous or solid products, and in some cases a low-melting solid fuel. There are two basic liquefaction processes, pyrolysis and dissolution.

Pyrolysis processes yield only low volumes of liquid fuel, along with large quantities of char, that would require further refinement. It is doubtful that pyrolysis systems will become a major source of petroleum (Epperley and Siegel, 1974).

Liquefaction by dissolution involves dissolving crushed coal in a solvent, filtering out the ash, and treating the liquid by hydrocracking. Once the solids are removed, the liquid can be catalytically upgraded. The solid ash can be used as fuel or for the production of hydrogen for the system. Hydrogen is used to remove the organic sulfur from the product that is not removed along with the ash.

Dissolution processes can be divided into three types: (1) systems that use neither catalyst nor hydrogen; (2) systems that use hydrogen but no catalyst; and (3) systems that use both hydrogen and a catalyst. The Solvent-Refined Coal (SRC) process is of the second type, whereas the H-Coal process employs both a catalyst and hydrogen.

The SRC-I process (fig. 2) produces a solid fuel containing less sulfur than the original feed coal and little or no ash regardless of the feed coal. The solvent-refined coal has a melting point of 300° to 400°F, and a heating value of approximately 16,000 BTU/lb. The SRC process can be divided into five steps:

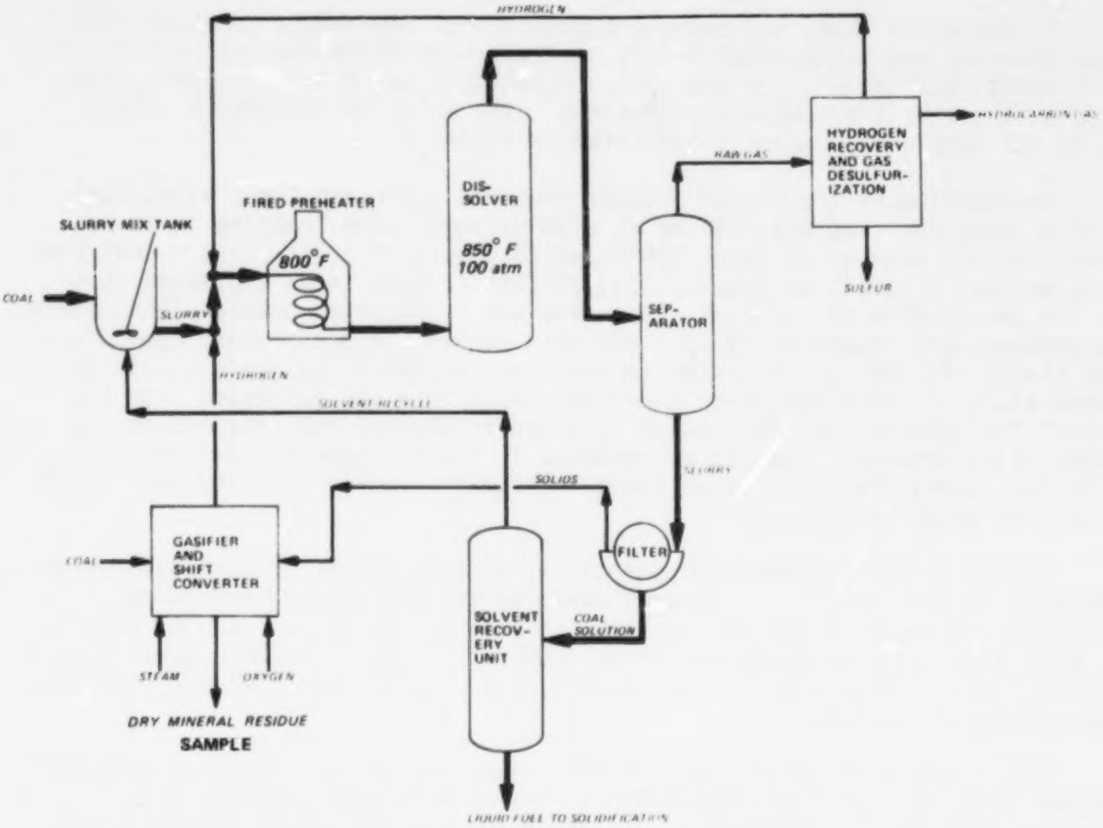
HYDROGEN
HYDROCARBON GAS
HYDROGEN RECOVERY AND GAS DESULFUR-IZATION
RAW GAS
SULFUR
FIRED PREHEATER
DIS-SOLVER
850° F
100 atm
SLURRY MIX TANK
800°F
COAL
SLURRY
SEP-ARATOR
HYDROGEN
SOLVENT RECYCLE
SLURRY
SOLIDS
GASIFIER AND SHIFT CONVERTER
COAL
FILTER
COAL SOLUTION
SOLVENT RECOV-ERY UNIT
STEAM
OXYGEN
DRY MINERAL RESIDUE
SAMPLE
LIQUID FUEL TO SOLIDIFICATION

Figure 2. SRC process schematic (White and Zahradnik, 1976).

1. The ground coal is mixed with a solvent that is derived from the process through a preheater to a dissolver maintained at 800° to 900°F and 1000 to 2000 psig. Approximately 90 percent of the organic material in the coal is dissolved.

2. The excess hydrogen is separated and cleaned by acid-gas absorption to remove hydrogen sulfide.

3. The slurry is filtered to remove the undissolved solids, which are then washed with a light solvent and dried.

4. The solvent is recovered from the filtrate by flash-distilling in a vacuum.

5. The distillation results in four fractions: a light liquid by-product, a wash solvent, a process solvent that can be recycled for use in the slurry, and a heavy residual product oil, termed solvent-refined coal.

In September 1976, we received a quantity of dry mineral residue from the Pittsburg and Midway Coal Mining Co. solvent-refined coal pilot plant at Fort Lewis, Washington, for analysis. A Kentucky No. 9 feed coal was being used at the time the sample was obtained. The point in the process from which the sample was taken is indicated in figure 2.

Dissolution by the H-Coal process requires slurrying the crushed coal with a heavy recycled oil, mixing it with hydrogen, and treating it in an ebullated bed reactor at about 850°F and 2500 psig (fig. 3). The H-Coal process employs a cobalt-molybdate catalyst that is kept in an ebullated state by the upward flow of the coal suspension and by hydrogen bubbles (Braunstein, Copenhaver, and Pfuderer, 1977). Hydrogen needed for the process comes from the slurry oil, which circulates through the reactor to maintain a constant temperature. Sulfur and ammonia are recovered from the gas taken from the top of the reactor, and the unused hydrogen is treated and returned to the dissolution process. The raw oil product is flashed down to low pressure, with the vapors distilled in an atmospheric distillation unit and the liquid distilled under vacuum.

Either a light synthetic crude oil or a heavy synthetic fuel oil can be produced by this process, depending upon the temperature and pressures involved. Because of the difficulties in separating the solids, the process is more applicable to production of a crude oil. Hydrocyclones, centrifuges, magnetic separators, and filters are all, for a variety of reasons, less than 100 percent efficient.

The solid waste sample used in this study was an unfiltered vacuum still bottom (fig. 3) from the H-Coal^R PDU at the Hydrocarbon Research Inc., Trenton, New Jersey, laboratory. At the time, the PDU was producing a fuel oil product from an Illinois Herrin (No. 6) feed coal.

ADDITIONAL COAL SOLID WASTES

In additional to the solid wastes collected from the conversion processes, six solid wastes from other forms of coal processing and utilization were studied. These included a fly ash and water-quenched bottom ash (slag) from a pulverized coal-fired power plant; the Illinois Herrin (No. 6) Coal was the power plant feed coal. Also, two coal-cleaning refuse samples—a low-sulfur and a high-sulfur gob—were analyzed. Again the Illinois Herrin (No. 6) Coal was the source.

The final samples were a medium-temperature char (1200°F) and a high-temperature char (1800°F). Both of these were prepared from the Illinois Herrin (No. 6) Coal using an electrically heated movable wall coke oven operated by the Illinois State Geological Survey in Urbana, Illinois. The medium-temperature char was prepared according to the American Society of Testing Materials standard method for testing the expansion or contraction of coal by the sole-heated oven (ASTM, 1973). Jackman et al. (1955) present a detailed discussion of the Survey's pilot coking plant and the procedure for making the high-temperature char.

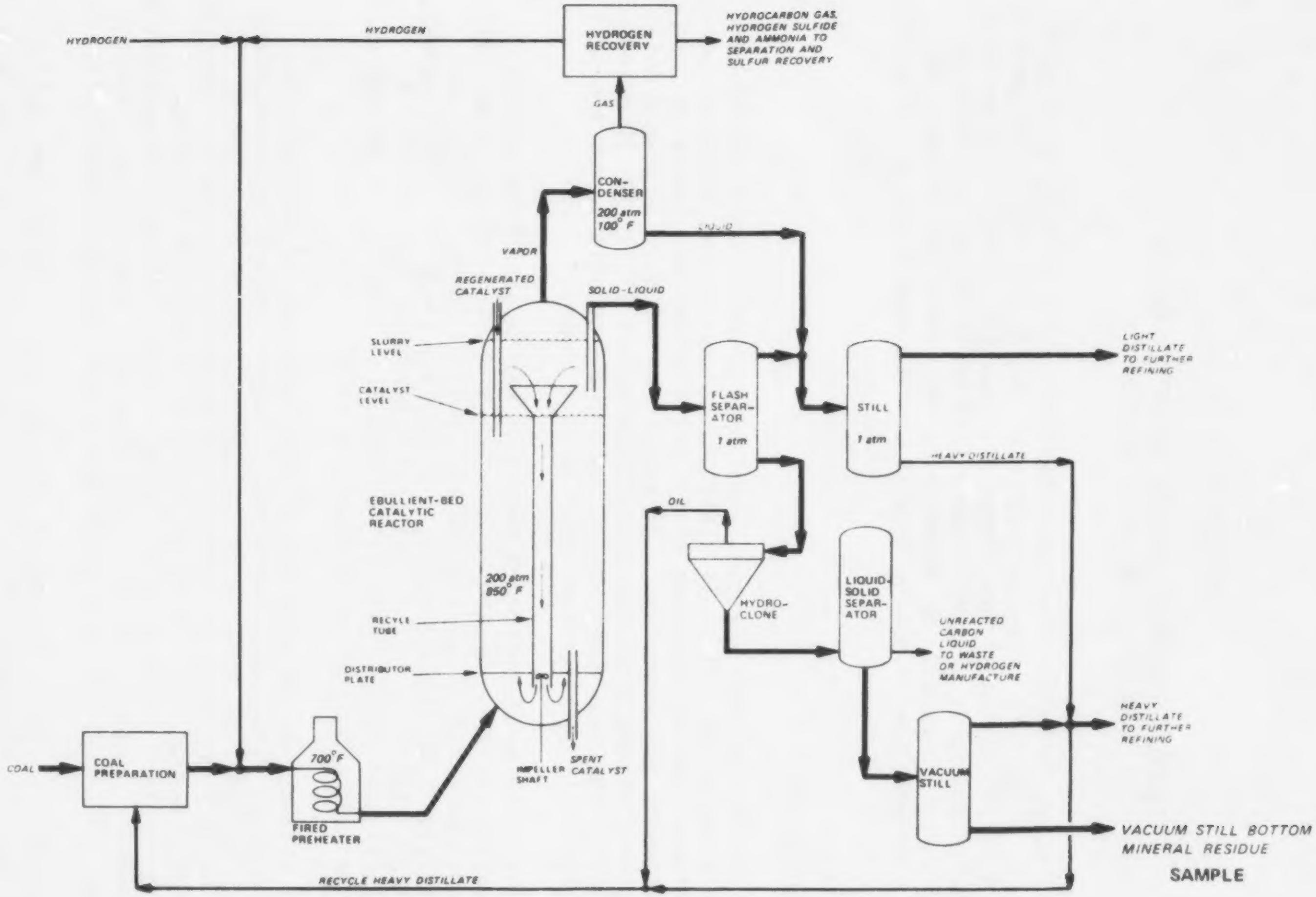
HYDROGEN
HYDROGEN
HYDROGEN RECOVERY
HYDROCARBON GAS, HYDROGEN SULFIDE AND AMMONIA TO SEPARATION AND SULFUR RECOVERY
GAS
CON-DENSER
200 atm
100° F
LIQUID
VAPOR
REGENERATED CATALYST
SOLID-LIQUID
SLURRY LEVEL
CATALYST LEVEL
FLASH SEPAR-ATOR
1 atm
STILL
1 atm
LIGHT DISTILLATE TO FURTHER REFINING
HEAVY DISTILLATE
EBULLIENT-BED CATALYTIC REACTOR
OIL
200 atm
850° F
HYDRO-CLONE
LIQUID-SOLID SEPAR-ATOR
UNREACTED CARBON LIQUID TO WASTE OR HYDROGEN MANUFACTURE
RECYLE TUBE
DISTRIBUTOR PLATE
HEAVY DISTILLATE TO FURTHER REFINING
COAL
COAL PREPARATION
700°F
IMPELLER SHAFT
SPENT CATALYST
VACUUM STILL
FIRED PREHEATER
VACUUM STILL BOTTOM
MINERAL RESIDUE
SAMPLE
RECYCLE HEAVY DISTILLATE

Figure 3. H-Coal process schematic (White and Zahradnik, 1976).

SECTION 5

MINERALOGICAL AND CHEMICAL CHARACTERIZATION OF THE COAL SOLID WASTES

The first stage in determining the potential pollution hazards of coal solid wastes was a complete characterization of the wastes, including both chemical and mineralogical analyses. These analyses are necessary to predict the total amounts and forms of constituents that could become available to the environment upon disposal. By determining the mineralogy of the feed coals, it is also possible to determine what changes take place during coal utilization.

ANALYTICAL PROCEDURES

Eleven solid wastes were analyzed chemically (over 60 constituents were determined) and mineralogically. In addition, 88 supernatant solutions generated by making 10 percent slurries of the solid wastes were analyzed for over 40 constituents and properties. An additional 360 solutions were collected from a soil attenuation study, and these were analyzed for 10 principal constituents. The supernatant solutions and the solutions from the soil attenuation study will be described later in this report.

The methods used to characterize the solid wastes were instrumental neutron activation analysis, neutron activation analysis with radiochemical separation, optical emission spectrochemical analysis (direct reading and photographic), atomic absorption analysis (flame and graphite furnace modes), x-ray fluorescence analysis, and ion-selective electrode procedures. A detailed discussion of sample preparation, detection limits, and procedures for these techniques can be found in Gluskoter et al. (1977).

Chemical analyses of the supernatant solutions, and of solutions from the soil attenuation experiments, were done by atomic absorption using flame and cold vapor methods, by ion-selective electrode, and by colorimetric techniques. The U.S. Environmental Protection Agency's "Methods for Chemical Analysis of Water and Wastes" (1974) was used as a reference for these techniques. Parameters measured by electrode included pH, oxidation-reduction potential, specific conductance, chlorides, fluorides, and sulfide. Ferrous iron, sulfate, orthophosphate, and boron were determined colorimetrically.

The mineralogical characterization employed x-ray diffraction, optical and scanning electron microscopy, and ^{57}Fe Mössbauer spectroscopic analysis (Bancroft, 1973). The x-ray diffraction and scanning electron microscopy techniques are explained in detail in Russell and Stepusin (1979). The procedures involved in Mössbauer spectroscopic analysis have also been cited in other literature (Smith et al., 1978).

MINERALOGICAL CHARACTERIZATION

Samples of the eleven wastes were analyzed by x-ray diffraction for mineralogical characterization and by Mössbauer spectroscopic analysis for determination of the iron species (table 2). Three feed coals were also characterized by x-ray diffraction: the Illinois Herrin (No. 6) Coal, the Harrisburg (No. 5) Coal, and the Montana Rosebud seam coal. The two Illinois coals were also analyzed by Mössbauer spectroscopy.

Using techniques applied in previous studies of coal (Smith et al., 1978), ash (Hinckley et al., 1979), and oil shale (Cole et al., 1978), the Mössbauer parameters were analyzed for the iron species in the coals and coal solid wastes (table 3). Each iron absorption was described in terms of Lorentzian curves with three parameters: isotope shift (S), quadrupole coupling constant (E), and internal magnetic field, when present (M).

Usually, the major iron-containing component in the Illinois No. 6 Coal was pyrite with a small amount of Fe^{+2} present in illite (Saporoschenko et al., 1979). Because this was a washed sample, some of the soluble iron-containing minerals such as sulfates may have been removed. Sulfates in coal are primarily oxidation products of pyrite that are formed when coal is exposed to moisture and the atmosphere.

In comparison, the major iron species in the Illinois No. 5 Coal was also pyrite, but ferrous sulfate rather than illite iron species were found. X-ray diffraction analysis, however, does show the presence of some illite in the coal.

The Rosebud coal exhibits two additional ferro-minerals—melanterite and goethite. This coal, however, was not studied with Mössbauer spectroscopy.

Spectra of Lurgi ash samples derived from the Illinois No. 5 and No. 6 Coals were very similar. Computer fitting of both spectra yielded seven multiplets that were assigned to six different iron species. These species were separated into two groups. The first group, iron oxides, included hematite, magnetite, and goethite (Hinckley et al., 1979; Dezsi and Fodor, 1966). All of these compounds had six line Mössbauer spectra characterized by magnetic hyperfine splitting. They accounted for 59 percent of the iron in No. 5 Coal ash and 56 percent in the No. 6 Coal ash. The second group contained the remaining three species, one ferric and two ferrous. These three species, which gave two line spectra, were iron ions in silicate and mullite.

Assignment of a Mössbauer absorption to an iron silicate species is a nonspecific identification because isotope shifts and quadrupole coupling constants vary widely for these species (Bancroft, Maddock, and Burnes, 1967). Iron silicate isotope shifts vary from 0.0 (measured vs. iron foil) to 0.5 mm/sec for Fe^{+3}, and from 1.0 to 1.4 mm/sec for Fe^{+2}. Quadrupole coupling

TABLE 2. MINERAL COMPOSITION OF COALS AND COAL SOLID WASTES

	Rose-bud	No. 6 (washed)	No. 5 (washed)	Fines (slurry)	Refuse (high-S gob)	Refuse (low-S gob)	Medium-temper-ature char	High-temper-ature char	H-Coal^{R}	Lurgi ash (No.6 coal)	Lurgi ash (No.5 coal)	Lurgi ash (Rose-bud)	Fly ash	SRC residue	Water-quenched slag
Nonferro minerals															
Sphalerite	—	X	X	—	—	X	—	—	—	—	—	—	—	—	—
Quartz	X*	X	X	X	X	X	X	X	X	X	X	X	X	X	—
Calcite	X	X	X	X	X	X	X	—	X	—	—	—	—	—	—
Dolomite	X	X	X	—	—	—	—	—	—	—	—	X	—	—	—
Anhydrite	X	X	X	X	—	—	X	—	—	—	—	—	X	—	—
Bassinite	X	—	—	X	—	—	—	—	—	—	—	—	—	—	—
Gypsum	X	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Kaolinite	X	X	X	X	X	X	—	—	X	—	—	—	—	X	—
Expandable clay	X	X	X	—	—	—	—	—	X	—	—	—	—	X	—
Feldspar	—	—	—	X	X	X	X	—	—	X	X	X	—	—	—
Wallastonite	—	—	—	—	—	—	—	—	SEM†	—	—	—	—	—	—
Ferro minerals															
Pyrite	X*	MX§	MX	MX	MX	X	MX	MX	—	—	—	—	—	—	—
Pyrrhotite	—	—	—	—	—	—	MX	MX	MX	—	—	—	—	MX	—
Illite‡	X	X	MX	MX	MX	MX	MX	MX#	—	—	—	—	—	—	—
Mullite‡	—	—	—	—	—	—	—	—	—	MX	MX	MX	—	—	—
Melanterite	X	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Fe^{+2}silicate	—	—	—	—	—	—	—	—	—	M	M	M	M	—	M
Hematite	—	—	—	—	—	—	—	—	—	MX	MX	MX	MX	—	—
Goethite	X	—	—	—	—	—	—	—	—	M	M	M	M	—	—
Magnetite	—	—	—	—	—	—	—	—	—	M	M	M	M	—	—
Hydrated ferrous sulfate	—	—	MX‖	—	MX‖	—	MX	MX	MX	—	—	—	—	MX	—
Ferrous carbonate	—	—	—	—	—	M	—	—	—	—	—	—	—	—	—

*X-ray analyses.

†Scanning electron microscope.

‡X-ray diffraction cannot distinguish between valence states of iron.

§M = Mössbauer analysis.

‖Anhydrous.

#Spinel group hercynite.

constants for iron silicates vary from 0.0 to 1.0 mm/sec for Fe^{+3}, and from 1.5 to 3.0 mm/sec for Fe^{+2}. The assignment means that silicate species are known to be present from x-ray and/or elemental analysis, that the assigned absorption is described by isotope shift and quadrupole coupling parameters that fall within the above ranges, and that these parameter values do not correspond to those of other known species.

Analysis of the Lurgi ash from Rosebud coal revealed that the oxides hematite, magnetite, and goethite were also present. This ash was similar to the ashes mentioned above, but differed in two important respects. First of all, 65 percent of the iron was present as oxide—a greater proportion than was present in the other two Lurgi ashes. Secondly, the oxide component assigned to goethite in the Rosebud Coal ash had a smaller magnetic field parameter than the goethite in the ashes from Illinois No. 5 and No. 6 Coals. Dezsi and Fodor (1966) observed Mössbauer multiplets for goethite characterized by small magnetic field parameters; they ascribed this to lattice imperfections. Consequently, since the nature of the lattice modifications are not known, this species is best described as goethite-like.

Nonoxide species were also similar to the other ashes in the study. Iron was distributed in mullite and silicate lattices. All of these species were insoluble because spectra of the ash as slurries in distilled water were essentially unchanged. In such an experiment, absorptions caused by soluble species are expected to show reduced or zero intensity in the wet sample.

The magnetite species in the three Lurgi ashes were not identified in the x-ray diffraction analyses because hematite, feldspar, and mullite—which interfere with the principal magnetite peaks—were present. Thus, the two techniques complement each other and allow identification of mineral species that could not be identified by one method alone.

The Lurgi ash samples included in this study are similar to the ashes derived from other oxidative processes (e.g. combustion), such as those obtained from a conventional power plant (Hinckley et al., 1979).

The liquefaction residues were also characterized mineralogically (tables 2 and 3). The major iron compound in the H-Coal^R sample identified from the Mössbauer spectrum was hexagonal pyrrhotite with a small amount of hydrated ferrous sulfate.

Pyrrhotite spectra in the H-Coal^R sample was unusual; magnetic parameters determined from this spectrum do not include the value 228 KOe found in both monoclinic and hexagonal pyrrhotite. Furthermore, a magnetic parameter value around 310 KOe was found in all of the samples containing pyrrhotite. This last value is characteristic of troilite, and suggests that the pyrrhotite in these materials is a mixture of troilite and iron-rich pyrrhotite (Schwarz and Vaugham, 1972; Novikov et al., 1977). X-ray analysis, however, indicates only pyrrhotite to be a component.

X-ray diffraction and Mössbauer analysis for the SRC-I dry mineral residue indicated that pyrrhotite was present (Keisch, Gibbon, and Akhtar, 1977/1978; Jacobs, Levinson, and Hart, 1978), along with hydrated ferrous sulfate.

TABLE 3. MÖSSBAUER PARAMETERS FOR IRON SPECIES IN COALS AND COAL SOLID WASTES

Assignment	S(mm/sec)	E(mm/sec)	M(KOe)	Fe* (%)
No. 6 coal (washed)				
Pyrite	0.305(8)	0.622(1)		99.8
Illite Fe^{+2}	1.26 (3)	2.79 (2)		0.2
No. 5 coal (washed)				
Pyrite	0.304(1)	0.618(1)		95.9
Ferrous sulfate	1.18 (2)	2.92 (3)		4.1
No. 6 coal slurry (fines)				
Pyrite	0.311(1)	0.652(1)		94.2
Illite Fe^{+2}	1.24 (2)	2.66 (4)		5.8
Refuse (high-sulfur gob)				
Pyrite	0.306(1)	0.616(1)		88.0
Illite Fe^{+3}	0.407(4)	1.142(4)		6.9
Illite Fe^{+2}	1.06 (2)	2.64 (4)		2.4
Ferrous sulfate	1.171(7)	2.956(8)		2.6
Refuse (low-sulfur gob)				
Illite Fe^{+3}	0.20 (1)	0.88 (2)		29.0
Illite Fe^{+3}	0.17 (3)	0.32 (9)		24.6
Illite Fe^{+2}	1.256(4)	2.56 (2)		29.3
Iron carbonate	1.38 (2)	1.59 (4)		17.0
Medium-temperature (650°C) char				
Pyrrhotite	0.788(8)	-0.230(4)	315(2)	7.8
Pyrrhotite	0.74 (1)	-0.04 (1)	305(3)	16.0
Pyrrhotite	0.735(8)	0.100(9)	274(4)	9.0
Pyrrhotite	0.73 (1)	0.24 (1)	251(4)	10.0
Pyrite	0.36 (1)	0.634(2)		48.0
Illite Fe^{+2}	0.999(9)	2.39 (2)		7.4
Ferrous sulfate (hydrated)	1.24 (1)	2.56 (2)		3.0
High-temperature (990°C) char				
Pyrrhotite	0.769(9)	-0.172(9)	313(2)	9.7
Pyrrhotite	0.758(9)	-0.05 (1)	304(3)	12.3
Pyrrhotite	0.727(7)	0.066(9)	277(4)	10.0
Pyrrhotite	0.76 (1)	0.13 (1)	247(5)	11.2
Pyrite	0.34 (1)	0.634(5)		49.3
Spinel group-hercynite	1.013(9)	2.26 (3)		4.5
Ferrous sulfate (hydrated)	1.32 (1)	2.44 (5)		3.0
H-Coal^{R}				
Pyrrhotite	0.78 (1)	-0.146(6)	311(6)	51.8
Pyrrhotite	0.82 (1)	0.048(9)	301(5)	7.8
Pyrrhotite	0.79 (1)	0.048(9)	287(5)	7.6
Pyrrhotite	0.75 (1)	0.144(8)	268(4)	30.2
Ferrous sulfate (hydrated)	1.24 (2)	2.59 (3)		2.6

TABLE 3. *Continued.*

Assignment	S(mm/sec)	E(mm/sec)	M(KOe)	Fe* (%)
Lurgi ash (No. 6 coal)				
Hematite	0.366(6)	-0.194(5)	511(2)	25.4
Magnetite	0.273(6)	0.004(2)	486(3)	7.9
Magnetite	0.609(4)	0.004(2)	453(3)	13.0
Goethite	0.658(4)	-0.03 (2)	383(4)	10.2
Fe^{+3} mullite	0.35 (3)	0.78 (3)		16.5
Fe^{+2} mullite	1.13 (2)	2.80 (3)		3.6
Fe^{+2} silicate	0.98 (2)	1.89 (2)		23.6
Lurgi ash (No. 5 coal)				
Hematite	0.369(6)	-0.194(5)	511(2)	27.2
Magnetite	0.268(6)	0.004(2)	487(2)	8.7
Magnetite	0.606(8)	0.004(2)	453(3)	13.8
Goethite	0.64 (4)	-0.05 (5)	385(3)	8.8
Fe^{+3} mullite	0.37 (2)	0.70 (4)		11.7
Fe^{+2} mullite	1.111(5)	2.76 (9)		5.0
Fe^{+2} silicate	1.000(6)	1.9 (1)		24.8
Lurgi ash (Rosebud)				
Hematite	0.366(6)	-0.180(5)	511(2)	25.2
Magnetite	0.274(6)	0.004(2)	486(2)	9.3
Magnetite	0.62 (2)	0.004(2)	453(3)	11.1
Goethite	0.65 (8)	-0.02 (2)	346(6)	11.1
Fe^{+3} mullite	0.36 (3)	0.80 (3)		12.4
Fe^{+2} mullite	1.128(8)	2.79 (1)		8.7
Fe^{+2} silicate	1.03 (1)	1.98 (2)		14.4
Fly ash power plant				
Hematite	0.363(4)	-0.204(5)	508(3)	13.0
Magnetite	0.322(4)	-0.04 (2)	483(3)	18.2
Magnetite	0.515(9)	-0.02 (1)	456(3)	10.8
Unassigned	0.542(9)	-0.06 (3)	429(6)	10.7
Goethite	0.50 (3)	-0.02 (1)	381(5)	10.4
Fe^{+3} silicate	0.99 (3)	2.02 (2)		9.9
Water-quenched slag				
Fe^{+3} silicate	0.190(7)	0.754(9)		2.8
	0.609(8)	1.028(2)		12.0
	1.064(6)	2.106(8)		27.9
Fe^{+2} silicate	1.029(5)	1.562(1)		40.0
	1.078(5)	2.628(1)		17.3
SRC residue				
Pyrrhotite	0.713(7)	0.11 (1)	302(6)	16.8
Pyrrhotite	0.750(9)	0.09 (2)	290(5)	11.8
Pyrrhotite	0.743(5)	0.09 (1)	268(4)	35.6
Pyrrhotite	0.693(9)	0.14 (2)	239(7)	16.4
Pyrite	0.370(6)	0.70 (1)		9.4
Ferrous sulfate (hydrated)	1.25 (1)	2.62 (2)		9.9

*Percentages are approximate values based on calculated areas of the absorption curves; they are relative to the iron species within each sample—not from one sample to another on a quantitative basis.

S = Isotope shift.

E = Quadrupole coupling constant.

M = Internal magnetic field (when present).

Mössbauer parameter values for pyrrhotite in this sample were different from those of the H-Coal^{R} and the chars in that they fell within ranges characteristic of the natural pyrrhotite from Sudbury in Ontario, Canada, which is often used as a standard of reference.

Sphalerite, calcite, anhydrite, and clay minerals were also identified in the H-Coal^{R} residue by x-ray diffraction. Wollastonite ($CaSiO_3$), undetected by x-ray diffraction, was found by a scanning electron microscope with an energy-dispersive x-ray analyzer in polished and etched samples of heavy minerals. Pyrrhotite, quartz, and clay minerals were identified in the SRC-I mineral residue by x-ray diffraction.

Mössbauer spectra of coarse refuse from a preparation plant using low-sulfur, Jefferson County Illinois (No. 6) Coal indicated that two ferric and two ferrous iron species were present. The two ferric and one of the ferrous species were assigned from the Mössbauer parameters to illite; the remaining ferrous species was assigned to an iron carbonate. X-ray diffraction data revealed traces of pyrite and melanterite in this sample, although it was not found in the Mössbauer analysis (tables 2 and 3).

The principal iron compound in the gob from high-sulfur No. 6 Coal was pyrite. The compound with the next highest percentage of iron was a ferric species which, together with one of the ferrous species, was assigned to illite. Ferrous sulfate was present in smaller quantities than the other species.

A coal slurry (fines) from the washing plant contained pyrite and illite. Nearly 6 percent of the iron found in the slurry was associated with illite, whereas only 0.2 percent of the iron found in the washed coal was associated with illite. Although hydrated ferrous sulfate was found in the slurry by x-ray diffraction analysis, it was not found by Mössbauer spectroscopy—perhaps because oxidation occurred during the time between the two analyses.

Results of Mössbauer and x-ray diffraction analyses of the medium- (650°C) and the high- (990°C) temperature chars indicate that pyrite was the principal iron compound in both chars (tables 2 and 3). Iron was found at concentrations of 46.8 percent and 49.3 percent, respectively, in the form of pyrite. Considerable concentrations (42.8 percent and 43.2 percent) of the iron was found in the form of pyrrhotite (Smith et al.,1978; Montano, 1977). In the low-temperature char, 7.4 percent of the iron was found in illite, whereas 4.5 percent of the iron was found in spinal (Hinckley et al, 1979) in the high-temperature char. Both x-ray diffraction analysis and Mössbauer spectroscopy showed the presence of hydrated ferrous sulfate in both chars. X-ray diffraction analysis of the two chars also indicated the presence of two calcium compounds—calcite and anhydrite—in the low-temperature char that were not present in the high-temperature char, but were evident in the Illinois No. 6 feed coal.

Fly ash from the power plant was different from the Lurgi ashes. For example, the oxide mixture contained more components more uniformly distributed than the Lurgi ashes. Fly ash contained only two mullite and silicate species; this difference was accentuated by an additional feature. In the

Lurgi ashes, ferrous iron (Fe^{+2}) accounted for 36 to 43 percent of the iron; whereas in the fly ash, ferrous iron accounted for only 24 percent of the iron.

The contrast between water-quenched molten bottom ash and fly ash samples was dramatic. The bottom ash contained no oxides. Species in the bottom ash were silicates (glasses); although four were identified (table 3), the relatively broad linewidth parameters suggested that more were probably present. Furthermore, most of the iron in the bottom ash was present as ferrous rather than ferric ions. The Fe^{+2}/Fe^{+3} ratio in bottom ash was 35.4, whereas in the fly ash and Lurgi ashes, the ratio ranged from 0.3 to 0.7.

Comparing the mineralogy of the coal solid wastes with that of the feed coals revealed that several chemical reactions took place during processing and conversion. For example, in the H-Coal^R process, a small amount of quartz and calcite reacted to form wollastonite. More importantly, nearly all the pyrite in the feed coal was converted to pyrrhotite in the solid waste. This occurred at temperatures lower than one would expect, based on data concerning reactions of pure iron sulfides at equilibrium conditions. These reactions could have occurred in the slurry preheaters or in the liquefaction process reactors. The pyrite-to-pyrrhotite conversion might have been a result of the cobalt-molybdate catalyst (which converts organic constituents to a fuel oil product in the H-Coal^R process), but the effect of the catalyst on the mineral interactions is not known. For example, in the SRC process, the change from pyrite to pyrrhotite also occurred without a catalyst; the SRC process does not use a catalyst.

In the two liquefaction processes studied, nearly all the pyrite in the feed coals was converted to pyrrhotite in the solid residues. This could have been caused by intimate association of the hydrogen in the liquefaction system with the pyrite in the coal slurry. Established phase relationships in closed systems cannot be directly applied to mineral matter in the liquefaction processes because of the undefined interactions of the components and the removal of vapor from the system during reactions. Mineral reactions must be deduced, therefore, from a thorough study of the coal mineral matter before and after coal conversion.

During the Lurgi gasification process, the pyrite in the feed coal was converted to hematite; this indicates that an oxidation process occurred during conversion. A similar change from pyrite to hematite took place in the power plant fly ash. The Fe^{+2}/Fe^{+3} ratios in the fly ash suggest that the oxidizing conditions in the power plant were more extreme than the conditions in the Lurgi process. Furthermore, hematite and magnetite are closely related substances. At high temperatures, magnetite is the more stable oxide; whereas below 1388°C, hematite is more stable (Deer, Howie, and Fussman, 1962).

Ferrous iron present as magnetite, therefore, reflects the ash's temperature history. On the other hand, ferrous iron present in silicate glasses more likely reflects oxidizing conditions. Ferrous iron was present in all samples in substantial amounts ($\sim$25 percent); thus, the Fe^{+2}/Fe^{+3} ratio determined by Mössbauer spectroscopy may be a useful factor to consider when following process conditions.

The two chars were similar mineralogically in that both contained pyrite and pyrrhotite, which indicated that an incomplete conversion occurred upon heating.

TABLE 4. MAJOR ELEMENTAL COMPOSITION AND ASH CONTENT OF THE SOLID WASTES

	Solid wastes										
Element	Lurgi No. 5 (%)	Lurgi No. 6 (%)	Lurgi Rosebud (%)	H-Coal (%)	SRC (%)	Fly ash (%)	Bottom ash (slag) (%)	High-temp. char (%)	Low-temp. char (%)	Low-S refuse (%)	High-S refuse (%)
Al	9.6	10.8	10.1	1.7	6.7	7.4	8.5	1.8	1.4	9.7	5.6
Ca	2.3	1.7	6.0	0.8	0.8	2.6	4.4	0.5	0.6	2.1	2.8
Fe	15.1	14.6	6.0	[illegible]	15.5	15.4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
K	1.3	1.5	0.5	0.2	0.9	2.1	1.3	0.3	0.4	1.7	1.0
Mg	0.4	0.4	2.2	<.1	<.1	0.4	0.5	2.9	0.8	0.4	0.2
Na	0.2	0.2	<.1	<.1	0.1	1.3	0.6	<.1	0.9	0.4	0.2
S	0.5	0.6	0.5	1.8	8.2	1.5	0.1	2.9	2.6	0.5	10.9
Si	24.6	23.0	22.6	4.0	11.1	19.4	22.3	4.0	5.0	26.1	14.5
Ti	0.6	0.6	0.6	0.1	0.2	0.5	0.4	<.1	0.4	0.8	0.5
Ash content	96.3*	94.6*	—	18.4	64.7	98.7	99.6	16.8	15.2	85.5	65.2

*Source: Sather et al., 1975

TABLE 5. MINOR ELEMENTAL CONSTITUENTS OF THE SOLID WASTES

	Solid wastes										
Element	Lurgi No. 5 (mg/kg)	Lurgi No. 6 (mg/kg)	Lurgi Rosebud (mg/kg)	H-Coal (mg/kg)	SRC (mg/kg)	Fly ash (mg/kg)	Bottom ash (slag) (mg/kg)	High-temp. char (mg/kg)	Low-temp. char. (mg/kg)	Low-S refuse (mg/kg)	High-S refuse (mg/kg)
B	465	355	810	300	100	200	—	400	300	200	9
Ba	760	950	3900	40	400	500	490	100	66	400	300
Ce	107	140	105	16	200	57	100	22	24	100	92
Cl	80	100	205	1000	400	28	100	200	400	700	300
Cr	171	212	55	28	100	100	130	29	25	78	45
F	<10	<10	300	100	500	100	133	92	100	900	1105
Mn	2014	1859	929	77	155	465	380	77	57	310	310
Sr	275	370	1500	30	600	200	310	13	<10	79	100
Zn	1500	400	31	71	13	62	560	48	42	500	300
Zr	185	170	251	—	100	200	200	36	28	200	100

CHEMICAL CHARACTERIZATION

Knowing which constituents are present in the solid wastes and in what concentrations is necessary to predict the maximum release of constituents during disposal; therefore, the chemical composition of the solid wastes was determined for over 60 constituents.

Generally, nine constituents were found in concentrations greater than 1000 mg/kg, or 0.1 percent of the solid wastes (table 4). These were Al, Ca, Fe, K, Mg, Na, S, Si, and Ti. Another group of minor constituents was found in concentrations generally greater than 100 mg/kg, but less than 1000 mg/kg (table 5). These included B, Ba, Ce, Cl, Cr, F, Mn, Sr, Zn, and Zr. Another 20 elements were found in concentrations less than 100 mg/kg (tables 7 to 17).

Correlation of the chemical characterization of the wastes from this study with characterizations from other investigations is difficult. The problem arises from the variability in the feed coals and the process parameters used—that is, changes in temperature and pressure will affect the fate of constituents and the nature of various waste streams. Table 6 shows the chemical analysis of two fly ashes collected at different times from the same coal-fired power plant. Although there are minor differences throughout, the major discrepancy is in the sulfur values. Whether the reduction in sulfur is caused by the use of a low-sulfur coal, or a cleaning process for coal pretreatment, or a change in operating conditions, is unknown.

TABLE 6. CHEMICAL COMPOSITION OF TWO FLY ASH SAMPLES FROM THE SAME POWER PLANT COLLECTED IN DIFFERENT MONTHS

Constituent	Fly ash I* (mg/kg)	Fly ash II (mg/kg)
Al	73,600	87,376
As	46	33
B	—	600
Ba	490	700
Be	16	10
Ca	26,100	29,413
Cr	130	100
Co	25	23
Cu	140	80
F	133	300
Fe_{Total}	134,400	147,212
K	20,900	17,268
La	34	51
Mg	3,500	4,100
Mn	380	387
Mo	67	10
Na	13,200	5,527
Ni	160	54
S_{Total}	14,900	800
Se	16	6
Si	194,300	226,925
Sr	310	200
Ti	5,100	5,096
Zn	560	600
Zr	200	200

*Fly ash I was used in the solubility, attenuation, and toxicity studies.

SECTION 6

AQUEOUS SOLUBILITY OF COAL SOLID WASTES

Leaching experiments have long been used to determine the soluble constituents of waste materials; however, research has only recently begun to focus on the importance of the vast array of variables inherent in these techniques (Ham et al., 1978; Wewerka et al., 1978). Three principal variables influence the design of a leaching experiment: (1) the duration of the leaching period; (2) the type of system to use—static or flowthrough; and (3) which experimental parameters will be set—e.g. temperature, pH, aerobic or anerobic. Because of the number of variables, the leaching experiment can be designed to suit the field situation that the investigator wishes to simulate.

A short shake test, which the U.S. EPA recommends for algal and static bioassays (1977), will put only the readily soluble salts into solution. A long-term test (over several months) would be more likely to allow equilibrium conditions to develop. Similarly, a long-term batch reactor test would permit the equilibration of large volumes of leachate. A column study, however, would allow for a more complete investigation of the rates of constituent solubility under the more variable conditions that would occur in a field situation. For example, the column test can be designed to study the different flow rates and volumes, along with the wetting and drying that simulates rainfall.

A variety of experimental parameters exist; the parameters chosen depend upon the field conditions to be simulated. These parameters include the size of the solid waste particles, the type of atmosphere (aerobic vs. anerobic) in which the system will be kept, the temperature of the leaching system, the method of agitation, and the use of a natural vs. adjusted pH for the system.

To determine the soluble constituents of the eleven coal solid wastes, large-volume, static leaching tests were used. This involved making 10 percent (weight to volume) slurries of solid waste and distilled water in 2½- and 5-gallon glass carboys. The subsequent bioassay and attenuation studies to be conducted with the leachates necessitated large volumes of leachate and rapid attainment of equilibrium. To attain equilibrium rapidly, the wastes were initially ground to pass through a 28-mesh sieve. This insured uniformity among the wastes, which in turn promoted a more rapid equilibrium than if larger sized particles were employed. The 10 percent slurry simulated a ponding type of disposal; it also facilitated attaining equilibrium conditions more rapidly than if higher percentage slurries were made, and made it easier to stir the large volumes of heavy slurries.

Duplicate series of four slurries were made for each solid waste. One slurry from each set was allowed to equilibrate to its natural pH, while the other three slurries in the set were adjusted by adding either nitric acid or sodium hydroxide to pH values over the range of 2 to 12. Over a period of 3 to 6 months, the slurries were stirred daily and their pH monitored or readjusted when necessary to a specified value. When a constant pH was attained, it was assumed that chemical equilibrium had been reached. Preliminary studies conducted with the Lurgi ashes indicated that over 90 percent equilibrium was attained within one week.

Out of the two sets of slurries for each waste, one was equilibrated under an argon (oxygen- and CO_2-free) atmosphere, and the other under an air atmosphere.

Probably the single most important factor affecting the solubility of the accessory elements in the coal solid wastes is pH. Many coal wastes contain sulfide minerals that can acidify upon exposure to air. Heavy metals contained in solid wastes disposed of in acidic strip or underground mines, are potentially more soluble than metals in wastes disposed of under neutral or alkaline conditions. To study the effect of pH on leaching of constituents from the wastes, it was desirable to maintain a range of pH levels in the slurries.

The oxidation-reduction potential (Eh) is also an important factor affecting the solubility of minerals (Garrels and Christ, 1965). When solid wastes are buried underground or in water-saturated materials, anaerobic (oxygen-deficient) conditions usually develop. Studies of the effects of Eh and pH on the solubilities of coal solid wastes could produce data that would allow the prediction of potential pollution hazards or, on the other hand, could predict which conditions would be optimum for extraction of the potentially valuable elements in the wastes.

RESULTS OF SOLUBILITY ANALYSIS

The supernatant solutions (leachates) from the equilibrated slurries were analyzed for 43 constituents. These concentrations plus the solid ash chemical characterizations are given in tables 7 through 17. Any values given with a less-than symbol (<) represent concentrations that could not be detected by the technique used for the analysis.

Several generalizations can be made about the soluble constituents generated from the solid wastes. As would be expected, the highest metal concentrations per any particular waste were found in the most acid supernatant solutions. A comparison of all the acid solutions shows that four constituents are at relatively high levels compared to recommended water quality criteria for all the waste solutions. (The recommended water quality criteria were based on values for the most sensitive likely use of the water recommended by the U.S. EPA in 1972.) These four constituents were Al, total Fe (both Fe^{+2} and Fe^{+3}), Mn, and Zn. The range of concentrations of these constituents was 6 to 510, 2 to 3000, 1 to 31, and 0.3 to 110 mg/L respectively.

TABLE 7. CHEMICAL COMPOSITION OF LURGI ASH AND SLURRY SUPERNATANT SOLUTIONS OF THE ASH FROM AN ILLINOIS NO. 5 COAL AT SEVERAL pH'S

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.25*	pH 8.90	pH 6.05	pH 3.09	pH 10.88*	pH 9.57	pH 6.25	pH 4.14
Ag	<.4	—	—	—	—	—	—	—	—
Al	95,506	<0.3	<0.3	<0.3	128	<0.3	<0.3	<0.3	24
Au	<.001	—	—	—	—	—	—	—	—
As	11	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
B	465	5.0	7.2	6.8	10.0	5.0	5.5	6.0	9.5
Ba	760	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Be	15	<.02	<.02	<.02	.05	<.02	<.02	<.02	<.02
Br	<1.0	—	—	—	—	—	—	—	—
Ca	22,571	470	560	660	970	410	550	680	1,060
Cd	<1.6	<.03	<.03	.05	.13	<.03	<.03	<.03	.05
Ce	107	—	—	—	—	—	—	—	—
Cl	80	<25	<25	<25	<25	<25	<25	<25	<25
COD†	—	2	2	2	2	10	2	4	86
MCE‡	—	7	20	23	1	—	—	—	—
Cr	171	.02	.04	.05	.04	.02	.03	.04	.10
Co	36	<.05	<.05	.12	.27	<.05	.06	.06	.16
Cu	50	.02	.04	.04	.30	.02	.03	.03	.07
Cs	10	—	—	—	—	—	—	—	—
Eu	1.7	—	—	—	—	—	—	—	—
F	<10	.16	.45	.35	.14	.28	.16	.35	.10
Fe_{Total}	151,016	.05	.10	.10	2.09	.11	.09	8.1	560
Fe^{+2}	—	.03	.04	.06	.75	.19	.10	.34	537
Ga	23	—	—	—	—	—	—	—	—
Ge	13	—	—	—	—	—	—	—	—
Hf	64	—	—	—	—	—	—	—	—
Hg	.05	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	12,867	30	31	32	38	29	29	33	44
La	49	—	—	—	—	—	—	—	—
Li	31	1.00	1.03	1.11	1.22	.90	.98	1.10	1.19
Lu	1.1	—	—	—	—	—	—	—	—
Mg	3,618	4.5	9.5	12	22	<.01	5	12	20

TABLE 7. *Continued.*

Constituents	Solid ash (mg/kg)	Chemical composition of 10% slurry supernatant: Air (mg/L) pH 8.25*	Air (mg/L) pH 8.09	Air (mg/L) pH 6.05	Air (mg/L) pH 3.09	Argon (mg/L) pH 10.88*	Argon (mg/L) pH 9.57	Argon (mg/L) pH 6.25	Argon (mg/L) pH 4.14
Mn	2,014	.05	.30	4.2	9.0	.01	.04	15.9	27.5
Mo	61	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Na	2,152	35	36	36	42	32	32	36	38
NH_4	—	12	14	11	3	12	10	15	16
Ni	195	.03	.06	.40	1.37	.03	.01	.14	.74
Pb	182	.1	.1	.2	.2	.1	.1	.1	.1
P	218	—	—	—	—	—	—	—	—
PO_4	—	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Rb	180	—	—	—	—	—	—	—	—
S_{Total}	5,400	—	—	—	—	—	—	—	—
S^{-2}	500	—	—	—	—	—	—	—	—
SO_4	8,400	623	665	670	492	650	480	300	210
Sb	2.8	.2	.4	.6	.7	.4	.4	.5	.9
Sc	23	—	—	—	—	—	—	—	—
Se	<2	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Si	245,653	34	23	24	125	30	14	18	88
Sm	8.2	—	—	—	—	—	—	—	—
Sn	—	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	2
Sr	275	1.3	1.8	2.1	2.8	1.3	1.8	2.0	2.5
Ta	0.9	—	—	—	—	—	—	—	—
Te	—	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th	19	—	—	—	—	—	—	—	—
Ti	6,415	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Tl	4.2	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
U	13	—	—	—	—	—	—	—	—
V	172	—	—	—	—	—	—	—	—
W	2.2	—	—	—	—	—	—	—	—
Yb	3.0	—	—	—	—	—	—	—	—
Zn	1,500	.03	.12	16.5	110	.01	.01	6	65
Zr	185	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	1.10	2.15	2.75	5.40	1.13	2.10	2.70	5.40
Fh (electrode mv)	—	+266	+273	+357	+440	+60	+133	-28	+180

* Natural pH of supernatant.

† Chemical oxygen demand.

‡ Methylene chloride extractable organics.

TABLE 8. CHEMICAL COMPOSITION OF LURGI ASH AND SLURRY SUPERNATANT SOLUTIONS OF THE ASH FROM AN ILLINOIS NO. 6 COAL AT SEVERAL pH'S

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 7.55*	pH 5.10	pH 3.82	pH 2.68	pH 8.82*	pH 7.20	pH 5.35	pH 3.79
Ag	<0.4	—	—	—	—	—	—	—	—
Al	108,121	<0.3	2	14	132	<0.3	<0.3	<0.3	92
Au	<.001	—	—	—	—	—	—	—	—
As	3	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
B	355	4.0	4.5	4.5	5.5	4.5	3.0	4.5	8.0
Ba	950	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Be	12	<.02	<.02	.01	.03	<.02	<.02	<.02	.01
Br	<1.0	—	—	—	—	—	—	—	—
Ca	16,652	290	480	400	570	440	370	430	500
Cd	<1.6	.02	.03	.03	.06	.01	<.03	.02	.05
Ce	140	—	—	—	—	—	—	—	—
Cl	100	<25	<25	<25	<25	<25	<25	<25	<25
COD[†]	—	2	2	2	81	2	2	16	140
MCE[‡]	—	28	28	0	23	10	3	6	4
Cr	212	<.02	.02	.05	.12	.01	.01	.06	.16
Co	34	<.05	.05	.08	.19	<.05	<.05	<.05	.17
Cu	57	.01	.02	.13	.73	.01	.05	.01	.05
Cs	11	—	—	—	—	—	—	—	—
Eu	1.9	—	—	—	—	—	—	—	—
F	<10	.31	.30	.09	.04	.51	.34	.16	.02
Fe_{Total}	143,780	.06	.19	.24	560	.06	.11	101	880
Fe^{+2}	—	.03	.11	.10	533	.13	.05	110	864
Ga	26	—	—	—	—	—	—	—	—
Ge	7.0	—	—	—	—	—	—	—	—
Hf	6.1	—	—	—	—	—	—	—	—
Hg	.05	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	14,611	42	49	51	26	39	43	48	61
La	47	—	—	—	—	—	—	—	—
Li	42	1.8	1.9	2.0	2.0	1.6	1.8	1.9	2.1
Lu	1.5	—	—	—	—	—	—	—	—
Mg	3,739	10.5	14	15	22	9.5	11	13.5	23

TABLE 8. *Continued.*

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 7.55*	pH 5.10	pH 3.82	pH 2.68	pH 8.82*	pH 7.20	pH 5.35	pH 3.79
Mn	1,859	.45	1.94	2.7	3.8	.11	.90	2.3	3.7
Mo	30	<.03	<.03	<.03	<.03	<.03	<.03	<.03	<.03
Na	1,929	34	37	38	40	32	37	37	40
NH_4	—	17	8	12	11	10	10	10	17
Ni	89	.03	.13	.23	.50	<.07	.04	.14	.42
Pb	45	.1	.1	.1	.2	.1	.1	.1	.2
P	87	—	—	—	—	—	—	—	—
PO_4	—	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Rb	162	—	—	—	—	—	—	—	—
S_{Total}	6,100	—	—	—	—	—	—	—	—
S^{-2}	1,500	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
SO_4	8.100	820	943	808	338	730	735	700	710
Sb	4.2	.2	.3	.3	.6	.3	.3	.3	.5
Sc	29	—	—	—	—	—	—	—	—
Se	<1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Si	229,946	5	29	60	130	4	9	27	120
Sm	8.21	—	—	—	—	—	—	—	—
Sn	—	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sr	370	1.8	1.9	2.1	2.9	1.5	1.7	1.9	2.6
Ta	1.1	—	—	—	—	—	—	—	—
Te	—	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th	21	—	—	—	—	—	—	—	—
Ti	6,295	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Tl	4.6	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
U	17	—	—	—	—	—	—	—	—
V	184	—	—	—	—	—	—	—	—
W	1.5	—	—	—	—	—	—	—	—
Yb	2.9	—	—	—	—	—	—	—	—
Zn	400	.12	5.5	12	17	.01	.11	6.5	20
Zr	170	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	1.17	1.50	1.95	5.60	1.20	1.39	1.80	5.20
Eh (electrode mv)	—	+223	+246	+407	+349	+109	+161	+102	+243

*Natural pH of supernatant.

†Chemical oxygen demand.

‡Methylene chloride extractable organics.

TABLE 9. CHEMICAL COMPOSITION OF LURGI ASH AND SLURRY SUPERNATANT SOLUTIONS OF THE ASH FROM A ROSEBUD COAL AT SEVERAL pH'S

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.44*	pH 8.14	pH 4.95	pH 3.13	pH 11.05*	pH 8.76	pH 5.26	pH 3.43
Ag	<.4	—	—	—	—	—	—	—	—
Al	101,188	<0.3	<0.3	7	510	<0.3	0.3	5	420
Au	.007	—	—	—	—	—	—	—	—
As	22	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
B	810	26.9	23.2	29.9	51.2	19.8	24.3	30.3	60.7
Ba	3,900	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Be	4.3	<.02	<.02	<.02	.08	<.02	<.02	<.02	.07
Br	<1.0	—	—	—	—	—	—	—	—
Ca	60,106	210	1,100	1,250	2,050	300	830	1,170	1,900
Cd	<1.6	.02	.02	.06	.06	<.02	.02	.03	.03
Ce	105	—	—	—	—	—	—	—	—
Cl	205	<25	<25	<25	<25	<25	<25	<25	<25
COD†	—	<1.0	2	2	45	11	7	12	110
MCE‡	—	26	11	16	41	—	—	16	—
Cr	55	.01	.05	.09	.14	.01	.03	.06	.20
Co	5.0	<.05	.08	.12	.20	<.05	.09	.10	.23
Cu	49	<.04	.02	.04	.54	<.04	.02	.03	.09
Cs	3	—	—	—	—	—	—	—	—
Eu	1.0	—	—	—	—	—	—	—	—
F	300	8.0	9.8	5.2	0.3	4.5	9.9	3.6	.25
Fe_{Total}	60,059	.01	.19	.15	300	.02	.06	86	670
Fe^{+2}	—	.03	.11	.05	275	.06	.06	59	633
Ga	24	—	—	—	—	—	—	—	—
Ge	8.2	—	—	—	—	—	—	—	—
Hf	12	—	—	—	—	—	—	—	—
Hg	.03	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	5,230	11	8	14	31	11	9	18	34
La	47	—	—	—	—	—	—	—	—
Li	65	.05	.58	.79	1.40	.36	.55	.77	1.40
Lu	.5	—	—	—	—	—	—	—	—
Mg	21,531	35	165	270	410	.9	160	260	440

TABLE 9. *Continued.*

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.44*	pH 8.14	pH 4.95	pH 3.13	pH 11.05*	pH 8.76	pH 5.76	pH 3.43
Mn	929	.04	1.06	16.2	26.5	.02	.97	15.7	28.0
Mo	29	.4	<.03	<.03	<.03	.6	.8	<.03	<.03
Na	74	10	14	16	34	10	11	26	32
NH_4	—	13	14	19	22	13	18	17	25
Ni	5	<.07	.05	.22	.50	<.07	.04	.17	.54
Pb	38	<0.1	.2	.3	.4	.1	.2	.2	.4
P	2,095	—	—	—	—	—	—	—	—
PO_4	—	<.01	<.01	<.01	<.01	<.01	<.01	<.01	2.38
Rb	46	—	—	—	—	—	—	—	—
S_{Total}	5,400	—	—	—	—	—	—	—	—
S^{-2}	1,100	—	—	—	—	—	—	—	—
SO_4	6,000	530	585	567	295	455	472	410	383
Sb	12	.4	1.0	1.2	1.3	.3	.9	1.1	1.2
Sc	15	—	—	—	—	—	—	—	—
Se	<3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3
Si	225,739	7	22	55	75	10	16	54	94
Sm	66	—	—	—	—	—	—	—	—
Sn	—	<1.0	<1.0	2	3	<1.0	1	2	2
Sr	1,500	3.4	9.0	14	26	4.1	9.2	14	26
Ta	1.7	—	—	—	—	—	—	—	—
Te	—	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	.5
Th	26	—	—	—	—	—	—	—	—
Ti	6,475	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Tl	2.0	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
U	8.0	—	—	—	—	—	—	—	—
V	30.8	—	—	—	—	—	—	—	—
W	5.4	—	—	—	—	—	—	—	—
Yb	1.8	—	—	—	—	—	—	—	—
Zn	31	<0.2	0.3	0.9	1.5	<0.2	.02	.58	1.3
Zr	251	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	.95	4.30	6.70	13.2	.91	4.10	6.50	14.0
Eh (electrode mv)	—	+216	+182	+259	+320	+45.05	+134	+130	+251

*Natural pH of supernatant.

†Chemical oxygen demand.

‡Methylene chloride extractable organics.

TABLE 10. CHEMICAL COMPOSITION OF H-COAL LIQUEFACTION WASTE AND SLURRY SUPERNATANT SOLUTIONS OF THE WASTE AT SEVERAL pH'S

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.83*	pH 8.16	pH 5.01	pH 3.14	pH 11.31*	pH 8.50	pH 5.53	pH 2.30
Ag	0.16	—	—	—	—	—	—	—	—
Al	17,253	3.0	<.5	<.5	5.5	1.5	<.5	1.5	5.7
Au	.01	—	—	—	—	—	—	—	—
As	1.5	<1	<1	<1	<1	<1	<1	<1	<1
B	300	11.0	13.0	11.6	13.6	11.0	12.2	12.9	15.0
Ba	40	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Be	1.8	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Br	6.7	—	—	—	—	—	—	—	—
Ca	7,862	110	175	380	497	133	155	425	487
Cd	<.4	<.03	<.03	<.03	<.03	<.03	<.03	<.03	<.03
Ce	16	—	—	—	—	—	—	—	—
Cl	1,000	75	71	67	75	78	70	75	64
COD[†]	—	15	9	9	15	24	8	2	24
Cr	27.5	<.02	<.02	<.02	.03	<.02	<.02	<.02	.05
Co	4.45	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Cu	14	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
Cs	1.7	—	—	—	—	—	—	—	—
Eu	0.69	—	—	—	—	—	—	—	—
F	100	1.00	1.15	0.60	0.86	0.70	1.20	0.85	0.84
Fe_{Total}	23,662	<.1	<.1	14	31.5	<.1	<.1	6.5	90
Fe^{+2}	—	<.1	<.1	11	29.5	<.1	<.1	.9	90
Ga	4.6	—	—	—	—	—	—	—	—
Ge	4.9	—	—	—	—	—	—	—	—
Hf	0.86	—	—	—	—	—	—	—	—
Hg	.05	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	2,490	1.4	1.4	2.1	2.8	1.2	1.5	2.0	2.5
La	9.8	—	—	—	—	—	—	—	—
Li	—	<.01	.01	.02	.02	<.01	.01	.02	.02
Lu	0.24	—	—	—	—	—	—	—	—
Mg	844	0.5	0.6	2.7	4.0	0.6	0.8	3.0	4.0

TABLE 10. *Continued.*

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.83[*]	pH 8.16	pH 5.01	pH 3.14	pH 11.31[*]	pH 8.50	pH 5.53	pH 2.30
Mn	77	<.02	.04	1.67	2.78	<.02	0.10	1.83	2.52
Mo	6.4	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Na	619	6.7	7.0	7.5	9.3	6.5	6.8	109[‡]	9.0
NH_4	—	9	6	8	8	8	5	7	5
Ni	21	<.07	<.07	<.07	<.07	<.07	<.07	<.07	.25
Pb	32	<0.1	<.1	.2	.25	<.1	<.1	.15	.2
P	44	—	—	—	—	—	—	—	—
PO_4	—	<.025	<.025	<.025	<.025	<.025	<.025	<.025	0.1
Rb	16	—	—	—	—	—	—	—	—
S_{Total}	18,000	—	—	—	—	—	—	—	—
S^{-2}	300	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
SO_4	600	65.5	68.5	148.5	96.5	65.5	66.0	70.5	73.5
Sb	1.2	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4
Sc	4.1	—	—	—	—	—	—	—	—
Se	3.0	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Si	39,641	<1	<1	<1	3	<1	<1	<1	3
Sm	2.3	—	—	—	—	—	—	—	—
Sn	0.6	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sr	30	.20	.24	.34	.50	.20	.26	.38	.48
Ta	0.17	—	—	—	—	—	—	—	—
Te	<0.1	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Th	3.5	—	—	—	—	—	—	—	—
Ti	1,019	<.6	<.6	<.6	<.6	<.6	<.6	<.6	<.6
Tl	1.7	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4
U	5.7	—	—	—	—	—	—	—	—
V	33	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
W	4.4	—	—	—	—	—	—	—	—
Yb	1.0	—	—	—	—	—	—	—	—
Zn	71	.01	.01	.06	.27	.02	.02	.12	.76
Zr	—	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	.44	.78	1.75	3.10	.68	.88	2.35	4.50
Eh (electrode mv)	—	+202.8	+235	+295.1	+419.6	+13.9	+178.9	+233.7	+100.0

[*] Natural pH of supernatant.

[†] Chemical oxygen demand.

[‡] NaOH added for pH adjustment.

TABLE 11. CHEMICAL COMPOSITION OF SRC LIQUEFACTION WASTE AND SLURRY SUPERNATANT SOLUTIONS OF THE WASTE FROM A KENTUCKY COAL AT SEVERAL pH'S

		Chemical composition of 10 slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 10.21	pH 6.35*	pH 4.69	pH 2.93	pH 9.66	pH 7.47*	pH 4.95	pH 3.00
Ag	.16	—	—	—	—	—	—	—	—
Al	67,529	4.0	<.5	<.5	27.0	3.0	<.5	<.5	23.5
Au	—	—	—	—	—	—	—	—	—
As	74	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
B	100	3.6	4.0	4.0	8.0	3.9	3.8	4.3	6.7
Ba	400	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Be	11	<.01	<.01	<.01	.14	<.01	<.01	.02	.07
Br	5.4	—	—	—	—	—	—	—	—
Ca	7,933	237	415	435	552	247	400	430	540
Cd	1.3	<.03	<.03	<.03	<.03	<.03	<.03	<.03	<.03
Ce	200	—	—	—	—	—	—	—	—
Cl	400	35	34	32	36	36	35	38	42
COD[†]	—	81	22	27	440	74	36	33	240
Cr	100	<.02	<.02	<.02	.65	<.02	<.02	<.02	.21
Co	32	<0.1	<0.1	<0.1	1.15	<0.1	<0.1	<0.1	0.15
Cu	100	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
Cs	5.8	—	—	—	—	—	—	—	—
Eu	3	—	—	—	—	—	—	—	—
F	500	0.44	0.09	0.04	0.07	0.06	0.24	0.09	0.10
Fe_{Total}	135,169	<.1	1.0	31.2	2,620	<.1	<.1	80	1,300
Fe^{+2}	—	<.1	1.9	2.8	2,500	<.1	<.1	62	1,220
Ga	15	—	—	—	—	—	—	—	—
Ge	18	—	—	—	—	—	—	—	—
Hf	2.36	—	—	—	—	—	—	—	—
Hg	.08	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	8,717	5.2	3.0	3.4	10.4	3.8	2.2	3.4	7.6
La	97	—	—	—	—	—	—	—	—
Li	—	.02	.04	.04	.12	.02	.03	.04	.11
Lu	0.78	—	—	—	—	—	—	—	—
Mg	60	0.6	2.5	2.9	8.0	1.2	2.2	2.9	7.5

TABLE 11. *Continued.*

Constituents	Solid ash (mg/kg)	Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
		pH 10.21	pH 6.35*	pH 4.69	pH 2.93	pH 9.66	pH 7.47*	pH 4.95	pH 3.00
Mn	155	<.02	.93	1.38	4.45	<.02	.66	1.58	4.20
Mo	21	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Na	1,461	340‡	9.0	9.0	18.0	230†	8.0	9.0	16.0
NH_4	—	9.0	10	10	24	10	11	10	16
Ni	14	<.07	<.07	.63	4.5	<.07	<.07	.33	.50
Pb	59	<.1	<.1	<.1	.2	<.1	<.1	<.1	.15
P	1,004	—	—	—	—	—	—	—	—
PO_4	—	<.025	<.025	<.025	.82	<.025	<.025	<.025	10.4
Rb	62	—	—	—	—	—	—	—	—
S_{Total}	82,400	—	—	—	—	—	—	—	—
S^{-2}	3,600	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
SO_4	9,600	1,030	1,025	1,187	1,324	940	945	875	975
Sb	8.2	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4
Sc	15	—	—	—	—	—	—	—	—
Se	20	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Si	110,930	<1	1.2	5	21	<1	1.2	4.5	18
Sm	17	—	—	—	—	—	—	—	—
Sn	6.2	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sr	600	2.34	2.72	2.76	5.36	2.10	2.64	2.68	4.80
Ta	.51	—	—	—	—	—	—	—	—
Te	1.3	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Th	14	—	—	—	—	—	—	—	—
Ti	1,799	<.6	<.6	<.6	<.6	<.6	<.6	<.6	<.6
Tl	9.3	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4
U	7.8	—	—	—	—	—	—	—	—
V	112	<.5	<.5	<.5	1.0	<.5	<.5	<.5	<.5
W	3.2	—	—	—	—	—	—	—	—
Yb	4.1	—	—	—	—	—	—	—	—
Zn	13.2	.02	.05	.86	5.6	.01	.02	.90	3.2
Zr	100	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	2.34	1.74	1.91	7.84	1.94	1.64	2.02	6.00
Eh (electrode mv)	—	-3.8	+198.4	+252.8	+271.5	+0.3	+41.5	+159.5	+225.0

*Natural pH of supernatant.

†Chemical oxygen demand.

‡NaOH added for pH adjustment.

TABLE 12. CHEMICAL COMPOSITION OF FLY ASH AND SLURRY SUPERNATANT SOLUTIONS OF FLY ASH FROM AN ILLINOIS NO. 6 COAL AT SEVERAL pH'S

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.82	pH 7.97	pH 4.08*	pH 2.74	pH 9.98	pH 7.08	pH 4.26*	pH 2.52
Ag	<1.8	—	—	—	—	—	—	—	—
Al	73,600	0.62	<0.3	62.6	419.0	4.12	<0.3	32.6	406.7
Au	—	—	—	—	—	—	—	—	—
As	46	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
B	600	40	46	58	62	44	52	57	64
Ba	490	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Be	16	<.02	.026	.052	.094	<.02	<.02	.043	1.03
Br	<3	—	—	—	—	—	—	—	—
Ca	26,100	130	435	508	879	401	449	506	872
Cd	<1.9	<.03	<.03	0.39	0.57	<.03	<.03	0.25	0.51
Ce	57	—	—	—	—	—	—	—	—
Cl	28	<25	<25	<25	<25	<25	<25	<25	<25
COD†	—	3	1	5	10	4	1	17	43
Cr	130	<.02	<.02	<.02	1.94	<.02	<.02	<.02	1.91
Co	25	<.05	<.05	0.31	0.44	<.05	<.05	0.25	0.50
Cu	140	<.04	<.04	0.20	0.84	<.04	<.04	<.04	0.95
Cs	11	—	—	—	—	—	—	—	—
Dy	9.3	—	—	—	—	—	—	—	—
Eu	1.6	—	—	—	—	—	—	—	—
F	133	1.5	1.4	2.5	0.16	1.2	0.72	3.0	0.13
Fe_{Total}	134,400	<.05	<.05	13.5	155	<.05	<.05	110	270
Fe^{+2}	—	<0.1	<0.1	9.0	87	<0.1	<0.1	92.5	210
Ga	51	—	—	—	—	—	—	—	—
Ge	15	—	—	—	—	—	—	—	—
Hf	3.9	—	—	—	—	—	—	—	—
Hg	0.05	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	20,900	36.0	10.2	1.4	10.8	56.0	17.0	1.1	16.1
La	34	—	—	—	—	—	—	—	—
Li	—	0.15	0.24	0.53	0.55	0.11	0.41	0.60	0.66
Lu	0.5	—	—	—	—	—	—	—	—

TABLE 12. *Continued.*

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.82	pH 7.97	pH 4.08*	pH 2.74	pH 9.98	pH 7.08	pH 4.26*	pH 2.52
Mg	3,500	0.28	33.0	46.1	53.9	0.05	40.9	44.9	54.3
Mn	380	.03	0.44	9.14	10.0	<.01	2.25	9.16	10.4
Mo	67	3.5	2.0	<0.3	<0.3	6.0	2.0	<0.3	<0.3
Na	13,200	367‡	281‡	195	220	415‡	271‡	185	230
NH_4	—	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.2	0.3
Ni	160	<.07	<.07	1.31	1.77	<.07	<.07	1.45	1.87
Pb	110	0.15	0.15	0.15	0.20	0.15	0.15	0.25	0.25
P	873	—	—	—	—	—	—	—	—
PO_4	—	<.01	.06	<.01	1.2	<.01	<.01	<.01	3.0
Rb	170	—	—	—	—	—	—	—	—
S_{Total}	14,900	—	—	—	—	—	—	—	—
S^{-2}	—	—	—	—	—	—	—	—	—
SO_4	—	3,650	3,150	2,350	3,100	4,950	3,250	2,250	3,450
Sb	3.5	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Sc	20	—	—	—	—	—	—	—	—
Se	16	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Si	194,300	1.33	4.0	35.0	95.5	2.0	6.67	22.7	93.5
Sm	7.7	—	—	—	—	—	—	—	—
Sn	11	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sr	310	0.27	0.16	2.0	3.15	0.55	0.16	1.58	3.48
Ta	1.2	—	—	—	—	—	—	—	—
Te	2.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th	12	—	—	—	—	—	—	—	—
Ti	5,100	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Tl	12	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
U	<12	—	—	—	—	—	—	—	—
V	230	<0.5	<0.5	<0.5	1.25	<0.5	<0.5	<0.5	3.0
W	6	—	—	—	—	—	—	—	—
Yb	2.6	—	—	—	—	—	—	—	—
Zn	560	.05	.03	20	15	.01	0.33	16	19
Zr	200	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	6.0	4.5	3.27	7.09	7.41	4.36	3.27	7.63
Eh (electrode mv)	—	+158.9	+215.5	+354.1	+474.1	+46.8	+200.3	+263.5	+390.1

*Natural pH of supernatant.

†Chemical oxygen demand.

‡NaOH added for pH adjustment.

TABLE 13. CHEMICAL COMPOSITION OF WATER-QUENCHED SLAG AND SLURRY SUPERNATANT SOLUTIONS OF THE SLAG FROM AN ILLINOIS NO. 6 COAL AT SEVERAL pH'S

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.82	pH 7.40	pH 3.81*	pH 2.83	pH 9.94	pH 8.30	pH 5.65*	pH 3.09
Ag	.80	—	—	—	—	—	—	—	—
Al	84,571	<.5	<.5	5.5	41.0	<.5	<.5	<.5	35.5
Au	—	—	—	—	—	—	—	—	—
As	2.7	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
B	200	<.5	<.5	<.5	<.5	<.5	<.5	<.5	0.6
Ba	500	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Be	2.4	<.01	<.01	<.01	<.01	<.01	<.01	<.01	.02
Br	0.6	—	—	—	—	—	—	—	—
Ca	43,668	7.0	9.5	17.5	33.5	5.0	9.7	12.0	31.0
Cd	<2	<.03	<.03	<.03	<.03	<.03	<.03	<.03	<.03
Ce	100	—	—	—	—	—	—	—	—
Cl	100	<20	<20	<20	<20	<20	<20	<20	<20
COD†	—	13	13	10	9.4	20	10	8.4	29
Cr	100	<.02	<.02	<.02	<.02	<.02	<.02	<.02	.06
Co	17.5	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Cu	40	<.05	<.05	.20	.32	<.05	<.05	<.05	.13
Cs	14.5	—	—	—	—	—	—	—	—
Eu	1.83	—	—	—	—	—	—	—	—
F	100	.07	.03	.04	.02	.06	.04	.02	.04
Fe_{Total}	137,267	.68	.17	.60	10.5	.55	.15	12.2	140
Fe^{+2}	—	<.1	<.1	<.1	1.8	<.1	<.1	11.0	125
Ga	12	—	—	—	—	—	—	—	—
Ge	0.33	—	—	—	—	—	—	—	—
Hf	6.88	—	—	—	—	—	—	—	—
Hg	.01	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	13,365	2.0	2.0	3.0	7.2	1.9	2.0	2.6	11.8
La	53	—	—	—	—	—	—	—	—
Li	—	<.01	<.01	.01	.03	<.01	<.01	<.01	.03
Lu	.87	—	—	—	—	—	—	—	—
Mg	5,066	0.6	1.3	2.2	4.0	0.2	0.9	1.4	3.8

TABLE 13. *Continued.*

Constituents	Solid ash (mg/kg)	Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
		pH 8.82	pH 7.40	pH 3.81*	pH 2.83	pH 9.94	pH 8.30	pH 5.65*	pH 3.09
Mn	465	.03	.06	.78	.95	.03	.05	.60	.85
Mo	2.8	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Na	5,935	98[‡]	44[‡]	2.1	4.9	45[‡]	20[‡]	1.6	4.8
NH_4	—	6.0	9.0	8.0	9.0	14	8.0	11	10
Ni	57	<.07	<.07	.13	.32	<.07	<.07	<.07	.13
Pb	20	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1
P	786	—	—	—	—	—	—	—	—
PO_4	—	<.025	<.025	<.025	<.025	.11	<.025	<.025	<.025
Rb	100	—	—	—	—	—	—	—	—
S_{Total}	1,100	—	—	—	—	—	—	—	—
S^{-2}	100	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
SO_4	1,200	97.5	101.5	80.5	109.0	50.5	52.5	51.0	28.5
Sb	4.2	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4
Sc	20	—	—	—	—	—	—	—	—
Se	<3	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Si	222,934	7	7	14.5	38	9	5.5	8	31.5
Sm	10.8	—	—	—	—	—	—	—	—
Sn	3.7	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sr	200	<.02	<.02	.04	.14	<.02	<.02	<.02	.16
Ta	1.2	—	—	—	—	—	—	—	—
Te	2.1	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Th	22	—	—	—	—	—	—	—	—
Ti	4,436	<.6	<.6	<.6	<.6	<.6	<.6	<.6	<.6
Tl	<4	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4
U	7.7	—	—	—	—	—	—	—	—
V	56	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
W	2.5	—	—	—	—	—	—	—	—
Yb	1.7	—	—	—	—	—	—	—	—
Zn	62	.02	<.01	.18	.28	<.01	<.01	.02	.28
Zr	200	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	0.55	0.33	0.32	1.00	0.24	0.18	1.64	1.26
Eh (electrode mv)	—	+244.3	+305.3	+462.1	+527.4	+89.9	+186.3	+310.3	+362.1

*Natural pH of supernatant.

[†] Chemical oxygen demand.

[‡] NaOH added for pH adjustment.

TABLE 14. CHEMICAL COMPOSITION OF CHAR (1800°F) AND SLURRY SUPERNATANT SOLUTIONS OF THE CHAR FROM AN ILLINOIS NO. 6 COAL AT SEVERAL pH'S

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.05*	pH 6.17	pH 4.33	pH 2.46	pH 7.45*	pH 7.26	pH 4.95	pH 3.03
Ag	.20	—	—	—	—	—	—	—	—
Al	17,147	<.5	<.5	<.5	27.0	<.5	3.0	31.5	—
Au	—	—	—	—	—	—	—	—	—
As	3.7	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	—
B	400	2.8	2.2	2.5	3.3	2.4	2.8	3.0	3.5
Ba	100	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Be	1.3	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Br	1.3	—	—	—	—	—	—	—	—
Ca	4,574	93	327	340	370	110	280	333	357
Cd	<0.5	<.30	<.30	<.30	<.30	<.30	<.30	<.30	<.30
Ce	22	—	—	—	—	—	—	—	—
Cl	200	<20	<20	<20	<20	<20	<20	<20	<20
COD†	—	41	6.8	60	190	31	16	30	71
Cr	28.9	<.02	<.02	<.02	.06	<.02	<.02	<.02	.04
Co	4.5	<0.1	<0.1	<0.1	0.25	<0.1	<0.1	<0.1	<0.1
Cu	14	<.05	<.05	<0.05	<.05	<.05	<.05	<.05	<.05
Cs	3.1	—	—	—	—	—	—	—	—
Eu	0.68	—	—	—	—	—	—	—	—
F	92	1.60	0.88	0.64	0.10	1.90	1.85	1.50	1.50
Fe_{Total}	23,951	<.1	.35	250	1,250	.15	<.1	100	415
Fe^{+2}	—	<.1	<.1	230	1,140	<.1	<.1	98	400
Ga	4.4	—	—	—	—	—	—	—	—
Ge	2.0	—	—	—	—	—	—	—	—
Hf	1.13	—	—	—	—	—	—	—	—
Hg	.01	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	2,656	2.0	2.8	4.0	8.6	1.4	2.0	4.2	9.4
La	8.4	—	—	—	—	—	—	—	—
Li	—	.03	.05	.06	.08	.03	.04	.05	.08
Lu	0.2	—	—	—	—	—	—	—	—
Mg	603	1.8	3.0	3.5	4.8	1.7	2.5	3.6	6.0

TABLE 14. *Continued.*

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.05[*]	pH 6.17	pH 4.33	pH 2.46	pH 7.45[*]	pH 7.26	pH 4.95	pH 3.03
Mn	77	.28	2.78	4.45	5.00	.58	1.80	2.52	4.85
Mo	4.1	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Na	953	3.5	16[‡]	6.0	8.5	3.0	4.0	6.1	8.4
NH$_4$	—	9.0	12	12	13	11	8.0	11	18
Ni	20	<.07	<.07	<.07	.20	<.07	<.07	<.07	<.07
Pb	12	<.1	.15	.2	.15	<.1	.15	.15	.15
P	87	—	—	—	—	—	—	—	—
PO$_4$	—	.025	.025	.025	1.95	.025	.025	.025	1.80
Rb	26	—	—	—	—	—	—	—	—
S$_{Total}$	28,700	—	—	—	—	—	—	—	—
S^{-2}	1,400	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
SO$_4$	300	100	219	69.5	106.5	77	73	33.7	30.7
Sb	0.44	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4
Sc	4.8	—	—	—	—	—	—	—	—
Se	4.1	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Si	40,015	4	4.3	7	27.5	5	6.5	20	34
Sm	1.9	—	—	—	—	—	—	—	—
Sn	0.9	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sr	13	.22	.42	.50	.68	.28	.40	.54	.64
Ta	0.33	—	—	—	—	—	—	—	—
Te	0.1	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Th	5.8	—	—	—	—	—	—	—	—
Ti	959	<.6	<.6	<.6	<.6	<.6	<.6	<.6	<.6
Tl	2.6	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4
U	2.0	—	—	—	—	—	—	—	—
V	20	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
W	0.63	—	—	—	—	—	—	—	—
Yb	2.0	—	—	—	—	—	—	—	—
Zn	48	<.01	.04	.38	.90	<.01	.02	.25	.62
Zr	36	—	—	—	—	—	—	—	—
Ec (mmhos/cm)	—	0.56	1.76	2.62	6.00	0.60	1.41	2.18	3.39
Eh (electrode mv)	—	+140.1	+195.8	+251.7	+353.3	-1.5	+66.9	+159.9	+188.6

[*] Natural pH of supernatant.
[†] Chemical oxygen demand.
[‡] NaOH added for pH adjustment.

TABLE 15. CHEMICAL COMPOSITION OF CHAR (1200°F) AND SLURRY SUPERNATANT SOLUTIONS OF THE CHAR FROM AN ILLINOIS NO. 6 COAL AT SEVERAL pH'S

		Chemical composition of 10% slurry supernatants							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 9.71	pH 7.19*	pH 3.81	pH 2.67	pH 9.72	pH 7.63*	pH 4.09	pH 2.42
Ag	.51	—	—	—	—	—	—	—	—
Al	13,601	2.18	<0.3	7.18	95.4	1.86	<0.3	3.46	89.4
Au	—	—	—	—	—	—	—	—	—
As	.17	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
B	300	11	10	9.1	10.5	12	8	12	8
Ba	66	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Be	1.2	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02
Br	4.0	—	—	—	—	—	—	—	—
Ca	6,075	2.0	207	283	306	2.0	141	285	294
Cd	0.4	<.03	<.03	<.03	<.03	<.03	<.03	<.03	<.03
Ce	24	—	—	—	—	—	—	—	—
Cl	400	72	72	71	75	72	77	75	76
COD†	—	5	2	6	5	5	4	7.5	126
Cr	24.5	<.02	<.02	<.02	<.02	<.02	<.02	<.02	.06
Co	3.4	<.05	<.05	<.05	0.13	<.05	<.05	<.05	0.15
Cu	11	<.04	<.04	<.04	0.31	<.04	<.04	<.04	0.24
Cs	3.4	—	—	—	—	—	—	—	—
Eu	.40	—	—	—	—	—	—	—	—
F^-	100	0.64	0.05	0.04	0.12	0.62	0.21	0.05	<.02
Fe_{Total}	5,860	.08	<.05	4.75	42.5	.10	<.05	29	780
Fe^{+2}	—	<0.1	<0.1	4.5	22.0	<0.1	<0.1	24	750
Ga	4.4	—	—	—	—	—	—	—	—
Ge	1.2	—	—	—	—	—	—	—	—
Hf	1.08	—	—	—	—	—	—	—	—
Hg	.01	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	3,321	5.5	3.7	9.5	20.1	5.4	2.7	9.0	19.1
La	8.1	—	—	—	—	—	—	—	—
Li	—	<.01	.03	.08	.18	<.01	.02	.07	0.17
Lu	.2	—	—	—	—	—	—	—	—
Mg	7,598	<.01	0.13	0.18	0.28	<.01	0.12	0.17	0.29

TABLE 15. *Continued.*

		Chemical composition of 10% slurry supernatants							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 9.71	pH 7.19*	pH 3.81	pH 2.67	pH 9.72	pH 7.63*	pH 4.09	pH 2.42
Mn	57	<.01	.57	3.2	4.3	<.01	.34	3.1	4.3
Mo	3.5	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Na	8,636	22.4[‡]	11.0	16.5	27.5	21.5[‡]	10.0	16.0	26.0
NH_4	—	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.1
Ni	12	<.07	<.07	0.16	0.34	<0.7	<0.7	0.19	0.34
Pb	8	<0.1	<0.1	<0.1	0.15	<0.1	0.15	0.15	0.30
P	87	—	—	—	—	—	—	—	—
PO_4	—	<.01	<.01	<.01	<.01	<.01	<.01	<.01	0.15
Rb	23	—	—	—	—	—	—	—	—
S_{Total}	25,800	—	—	—	—	—	—	—	—
S^{-2}	900	—	—	—	—	—	—	—	—
SO_4	1,600	655	500	955	200	530	170	860	175
Sb	.38	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Sc	2.4	—	—	—	—	—	—	—	—
Se	3.3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Si	50,490	3.33	5.00	23.0	48.7	3.33	4.33	19.3	48.3
Sm	1.9	—	—	—	—	—	—	—	—
Sn	3.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sr	<10	<.05	0.55	0.68	0.93	<.03	0.49	0.74	0.90
Ta	.3	—	—	—	—	—	—	—	—
Te	1.3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th	4.9	—	—	—	—	—	—	—	—
Ti	4.318	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Tl	2.6	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
U	1.8	—	—	—	—	—	—	—	—
V	21.8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
W	.63	—	—	—	—	—	—	—	—
Yb	1.2	—	—	—	—	—	—	—	—
Zn	42	.02	.02	0.59	1.0	<.02	.08	0.28	0.66
Zr	28	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	2.56	1.04	1.42	3.71	3.16	0.75	1.42	6.32
Eh (electrode mv)	—	+134.3	+258.0	+362.6	+491.2	+83.5	+181.0	+321.1	+358.2

*Natural pH of supernatant.

[†] Chemical oxygen demand.

[‡] NaOH added for pH adjustment.

TABLE 16. CHEMICAL COMPOSITION OF HIGH-SULFUR CLEANING WASTE (GOB) AND SLURRY SUPERNATANT SOLUTIONS OF THE GOB FROM AN ILLINOIS NO. 6 COAL AT SEVERAL pH'S

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.34	pH 7.45*	pH 3.43	pH 2.63	pH 8.89	pH 7.41*	pH 3.81	pH 2.53
Ag	.20	—	—	—	—	—	—	—	—
Al	56,522	<0.3	<0.3	4.7	27.6	<0.3	<0.3	5.28	35.3
Au	—	—	—	—	—	—	—	—	—
As	13	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
B	9.3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Ba	300	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Be	2	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02
Br	1.2	—	—	—	—	—	—	—	—
Ca	28,159	21.8	480	2,062	2,310	13.8	590	2,079	2,305
Cd	<1.4	<.03	<.03	.07	.08	<.03	<.03	.07	.09
Ce	92	—	—	—	—	—	—	—	—
Cl	300	28	28	33	33	28	28	30	33
COD[†]	—	7	5	3	32	6	3	8	45
Cr	45.3	<.02	<.02	.06	.09	<.02	<.02	<.02	.07
Co	10.3	<.05	<.05	.48	.90	<.05	<.05	.48	.82
Cu	29	<.04	<.04	.07	.09	<.04	<.04	<.04	.07
Cs	9.6	—	—	—	—	—	—	—	—
Eu	1.2	—	—	—	—	—	—	—	—
F	1,105	1.40	0.47	1.40	0.23	1.40	0.50	1.70	0.40
F_{Total}	86,157	<.05	<.05	1.2	205	<.05	<.05	26.5	275
Fe^{+2}	—	<0.1	<0.1	0.6	195	<0.1	<0.1	20	243
Ga	11	—	—	—	—	—	—	—	—
Ge	1.2	—	—	—	—	—	—	—	—
Hf	3.24	—	—	—	—	—	—	—	—
Hg	.02	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	9,962	11.4	11.9	15.6	19.4	10.1	15.5	16.0	20.5
La	43	—	—	—	—	—	—	—	—
Li	—	.03	.07	.12	.18	.03	.08	.11	.16
Lu	.34	—	—	—	—	—	—	—	—
Mg	1,869	.09	0.95	59.1	6.87	.08	1.0	58.3	70.4

TABLE 16. *Continued.*

		Chemical composition of 10% slurry supernatants							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 8.34	pH 7.45*	pH 3.43	pH 2.63	pH 8.89	pH 7.41*	pH 3.81	pH 2.53
Mn	310	<.01	1.83	14.7	17.4	<.01	2.05	14.5	18
Mo	3.2	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Na	2,419	475‡	170	175	180	460‡	185	165	175
NH_4	—	0.2	0.3	1.8	3.8	0.3	1.5	2.9	4.2
Ni	48	<.07	<.07	1.23	1.45	<.07	<.07	1.30	1.57
Pb	55	<0.1	0.2	0.4	0.4	0.15	0.2	0.45	0.5
P	829	—	—	—	—	—	—	—	—
PO_4	—	<.01	<.01	<.01	2.0	<.01	<.01	<.01	13.5
Rb	100	—	—	—	—	—	—	—	—
S_{Total}	108,800	—	—	—	—	—	—	—	—
S^{-2}	76,100	—	—	—	—	—	—	—	—
SO_4	13,500	2,000	1,600	1,200	1,300	1,800	1,500	1,000	1,400
Sb	.2	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Sc	9.1	—	—	—	—	—	—	—	—
Se	12.6	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Si	145,490	<1.0	1.70	12.0	37.1	<1.0	1.70	12.7	35.7
Sm	6.9	—	—	—	—	—	—	—	—
Sn	3.3	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sr	100	0.3	2.0	3.84	4.66	0.27	2.93	4.79	7.29
Ta	.8	—	—	—	—	—	—	—	—
Te	.6	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th	13	—	—	—	—	—	—	—	—
Ti	4,668	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Tl	8.2	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
U	2.9	—	—	—	—	—	—	—	—
V	35.3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
W	2.5	—	—	—	—	—	—	—	—
Yb	2.1	—	—	—	—	—	—	—	—
Zn	300	.02	<.01	.46	3.7	<.01	<.01	.47	3.1
Zr	100	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	3.8	2.4	7.6	11.0	3.4	2.4	7.4	10.9
Eh (electrode mv)	—	+190	+223.1	+502.6	+386	+63.2	+158.1	+303	+333.5

*Natural pH of supernatant.

†Chemical oxygen demand.

‡NaOH added for pH adjustment.

TABLE 17. CHEMICAL COMPOSITION OF LOW-SULFUR CLEANING WASTE (GOB) AND SLURRY SUPERNATANT SOLUTIONS OF THE GOB FROM AN ILLINOIS NO. 6 COAL AT SEVERAL pH'S

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 9.19	pH 7.79*	pH 3.50	pH 2.54	pH 9.24	pH 7.21*	pH 4.88	pH 2.43
Ag	.30	—	—	—	—	—	—	—	—
Al	97,008	4.4	<0.3	8.53	29.0	0.62	<0.3	<0.3	57.0
Au	—	—	—	—	—	—	—	—	—
As	68	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
B	200	1.0	<0.5	<0.5	<0.5	1.0	<0.5	<0.5	<0.5
Ba	400	<0.1	0.72	2.54	1.90	<0.1	1.64	1.82	2.54
Be	3	<.02	<.02	<.02	.034	<.02	<.02	<.02	.034
Br	3.2	—	—	—	—	—	—	—	—
Ca	21,227	4.6	568	2,287	2,595	4.6	943	1,973	2,784
Cd	1.8	<.03	<.03	.08	.09	<.03	.04	.08	.09
Ce	100	—	—	—	—	—	—	—	—
Cl	700	30	28	28	34	30	28	28	34
COD[†]	—	10	6	12	26	4	9	11	61
Cr	78	<.02	<.02	<.02	.06	<.02	<.02	<.02	0.13
Co	13	<.05	<.05	.45	.64	<.05	<.05	.27	.48
Cu	36	<.04	<.04	.28	1.68	<.04	<.04	<.04	1.34
Cs	15.2	—	—	—	—	—	—	—	—
Eu	1.5	—	—	—	—	—	—	—	—
F^-	900	1.7	.94	2.2	1.9	1.7	1.1	1.1	.48
Fe_{Total}	24,813	1.1	1.08	10	130	1.2	.08	2.2	360
Fe^{+2}	—	<0.1	<0.1	2.3	52	<0.1	<0.1	0.5	285
Ga	19	—	—	—	—	—	—	—	—
Ge	4.1	—	—	—	—	—	—	—	—
Hf	7.94	—	—	—	—	—	—	—	—
Hg	.05	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	17,102	4.5	17.8	29.0	38.0	3.0	20.0	25.0	40.0
La	50	—	—	—	—	—	—	—	—
Li	—	<.01	.07	.16	.26	<.01	.09	.15	.33
Lu	.42	—	—	—	—	—	—	—	—
Mg	3,859	.02	0.79	80.0	119.7	.05	30.0	68.7	138.9

TABLE 17. *Continued.*

		Chemical composition of 10% slurry supernatants							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid ash (mg/kg)	pH 9.19	pH 7.79*	pH 3.50	pH 2.54	pH 9.24	pH 7.21*	pH 4.88	pH 2.43
Mn	310	.02	.59	12.6	24.4	.07	2.06	9.9	30.7
Mo	<1	—	—	—	—	—	—	—	—
Na	3,635	485‡	245	250	250	505‡	260	245	255
NH_4	—	<0.1	1.8	3.9	4.5	<0.1	1.8	4.0	4.9
Ni	55	<.07	<.07	.69	1.06	<.07	<.07	.33	.85
Pb	55	.15	.15	.40	.50	<0.1	.20	.40	.70
P	1,397	—	—	—	—	—	—	—	—
PO_4	—	.08	.04	14.5	3.0	.06	2.75	3.25	44.0
Rb	200	—	—	—	—	—	—	—	—
S_{Total}	5,100	—	—	—	—	—	—	—	—
S^{-2}	4,600	—	—	—	—	—	—	—	—
SO_4	400	43	96	73	67	24	60	49	45
Sb	2.7	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Sc	15.2	—	—	—	—	—	—	—	—
Se	3.3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Si	261,380	19.3	13.7	64.6	96.2	15.0	25.3	55.0	116.5
Sm	8.0	—	—	—	—	—	—	—	—
Sn	7.2	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sr	79	.03	2.60	7.06	8.00	.03	3.70	6.83	9.12
Ta	1.2	—	—	—	—	—	—	—	—
Te	2.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th	20	—	—	—	—	—	—	—	—
Ti	8,298	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Tl	8.0	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
U	3.1	—	—	—	—	—	—	—	—
V	39.8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
W	2.9	—	—	—	—	—	—	—	—
Yb	4.3	—	—	—	—	—	—	—	—
Zn	500	.16	<.01	.27	1.55	2.25	.06	.12	1.40
Zr	200	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	.74	4.4	9.3	12.1	.71	5.4	8.5	12.5
Eh (electrode mv)	—	+122	+189.8	+314.1	+404.7	+53.4	+168.4	+210.4	+319.8

*Natural pH of supernatant.

†Chemical oxygen demand.

‡NaOH added for pH adjustment.

Calcium values exceeded the recommended levels for all but the slag acid leachate; however, although several of the calcium concentrations were in the range of 1000 to 2000 mg/L, they did not present the environmental hazard that the four constituents mentioned above do. Additional trace metals were found in some of the most acid leachates at concentrations slightly above the recommended levels for certain water types. They were not found in solution at detectable concentrations in the intermediate acid leachates (pH 5.5 to 4.0). Boron was present in amounts exceeding the recommended level for irrigation water (0.75 mg/L) in all but two of the most acid leachates, and over the entire pH range in eight of the slurry sets. The current assessment of boron's effect on the environment, however, leaves some question as to whether the boron concentrations found in this study are hazardous to the environment.

Sulfate was the dominant anion in solution with concentrations that ranged as high as 5000 mg/L. Sulfate, however, along with Cl, K, and Na, showed no pH dependency in their solubility.

Nonetheless, the most easily leached constituent does not always possess the greatest potential for pollution. Although, under acid conditions, many constituents exceeded the U.S. EPA recommended levels, it was felt that those that exceeded the recommended levels over the entire pH range had the greatest potential for pollution. Table 18 lists those constituents that were found to exceed the recommended levels over the pH range studied (including both aerobic and anaerobic solutions), and under the laboratory conditions described earlier. Also included in table 18 is a summary of the pH ranges for the supernatant solutions for each waste along with the natural (unadjusted) pH for both the aerobic and the anaerobic series.

TABLE 18. ELEMENTS WITH CONCENTRATIONS EXCEEDING RECOMMENDED WATER QUALITY LEVELS UNDER THE LABORATORY TEST CONDITIONS

		Natural pH		
Sample	pH range	Air	Argon	Constituents
Lurgi Ash (Ill. #6 Coal)	8.8-2.7	7.6	8.8	B, Ca, Cd, K, Mn, NH_4, Pb, SO_4, Sb
Lurgi Ash (Ill. #5 Coal)	10.9-3.1	8.3	10.9	B, Ca, K, Mn, NH_4, Pb, SO_4, Sb
Lurgi Ash (Rosebud Coal Mont.)	11.1-3.1	8.4	11.1	B, Ca, Cd, F, K, Mo, NH_4, Pb, SO_4, Sb
SRC	10.2-2.9	6.4	7.5	B, Ca, Fe, Mn, NH_4, SO_4
H-Coal	11.3-2.3	8.8	11.3	B, Ca, NH_4
Char (1200°F)	9.7-2.4	7.2	7.6	B
Char (1800°F)	8.1-2.5	8.1	7.5	B, Ca, Mn, NH_4
Low-sulfur gob	9.2-2.4	9.2	9.2	None
High-sulfur gob	8.9-2.5	7.5	7.4	K, NH_4, SO_4
Slag	8.8-2.8	3.8	5.7	NH_4
Fly ash	10.0-2.5	4.1	4.3	B, Ca, SO_4

The two most important factors affecting the solubility of minerals were probably the pH and the redox potential. The solid waste that has the lowest pH value would also pose the greatest potential threat to the environment. Indeed, the power plant slag and fly ash natural leachates appear to present greater hazards because of their dissolved constituents than the natural pH leachates from the other wastes. The experimental conditions described above, however, may not have been as conducive as natural conditions to the development of naturally acid pH's for several of the other wastes, such as the gob samples.

There is reason to believe that using 10 percent slurries in large volumes may prohibit complete oxidation of the iron sulfides in several of the solid wastes because of oxygen's slow diffusion rate through water. Complete oxidation would result in sulfuric acid production and a lowering of pH, along with a subsequent increase in constituent solubility for those wastes containing an appreciable amount of pyrite. Under different experimental conditions, therefore, the natural pH's of some of the waste leachates may be greatly decreased. It was felt that pH adjustment to the low values in table 18 helps to simulate the acid conditions that may develop under different environmental conditions.

Comparison of the constituent concentrations of the two sets of slurries for each waste was difficult because the sets were equilibrated to slightly different pH values for the air and argon slurries. Although it was attempted to pair the pH values between the sets of slurries, the values often varied by as much as 0.5 pH units. The iron concentrations were instructive in cases where the acid pH's were similar: generally, the leachates equilibrated under argon exhibited higher concentrations of iron (predominantly ferrous iron) in solution—especially at the intermediate acid pH level (5.5 to 4.0). Undoubtedly this was caused by the lack of available oxygen in the slurries equilibrated under argon. Similar results could be expected for several other metals present.

Table 18 also indicates that the soluble constituents found in solid wastes were similar for the same treatment no matter which feed coal was used; i.e., the three Lurgi ashes yielded nearly the same major soluble constituents for all three feed coals. The same was true for the two liquifaction wastes. The Illinois No. 6 Coal was used in both the Lurgi and H-Coal processes, but quite different soluble constituents were derived from the wastes. The Cd, K, Mn, Na, Pb, SO_4, and Sb found in the Lurgi ash leachates indicated that they were more soluble than those same constituents from the H-Coal residue under the conditions used.

SECTION 7

EQUILIBRIUM SOLUBILITY MODELING OF THE LEACHATES FROM COAL SOLID WASTES

The application of equilibrium solubility models can lead to useful insights into the chemistry of aqueous systems. Equilibrium models provide, at a minimum, boundary conditions within which questions may be framed. For example, a typical environmental problem solved by equilibrium models is that of predicting what is the highest concentration of a given constituent that can be achieved in solution before precipitation occurs with a given solid phase. Solutions to such problems can be sueful in developing a "worst case" scenario for a given pollutant that is leaching from a solid waste, by setting the upper boundary for concentrations of the pollutant that will have to be dealt with under a given set of conditions.

The results of applications of solubility models to environmental problems must be interpreted carefully. For example, it is not uncommon to find large discrepancies in literature values for the solubility products of some mineral phases. The value of the solubility product may depend on the direction of approach to equilibrium, the use of well-defined crystals versus precipitation, and phenomena such as phase transitions, aging, colloid formation, and differences in particle size. These factors, along with slow attainment of equilibrium and the fact that impure minerals are found in nature as opposed to the pure minerals used to determine solubility constants, may obscure solubility relationships and their application to practical environmental problems.

Important factors controlling the solubility of mineral phases include pH, the redox environment of the system, the oxidation state of the mineral components, the concentration and speciation of individual inorganic and organic ions and complexes in solution, and the ionic strength (total soluble ions). Applying the results obtained from solubility models to real environmental conditions requires considerable caution; nevertheless, assuming that the activities are calculated correctly and that the equilibrium constants are numerically factual, these models should accurately predict the solubility of an ion under a given set of conditions for a long list of solid phases.

EQUILIBRIUM SOLUBILITY MODEL

Explaining the aqueous chemistry of a complex system such as the leachates from coal conversion solid wastes is diffucult. Possible complexation, ion pair formation, and the effects of organic components on the formation of organo-metallic complexes hinders the description of these systems. On the other hand, it is still important to examine these systems and account for their soluble components, and we progress if we prepare diagrams showing the relations of the known aqueous species to the mineral solid phases.

Solubility and mineral stability diagrams were prepared according to Garrels and Christ (1965). The thermodynamic solubility model used in this study (WATEQF) considered the speciation of 115 aqueous inorganic ions and complexes and computed saturation data for over 100 minerals. The theory of the model and its computer implementation have been discussed previously by Truesdell and Jones (1973; 1974) and Plummer, Jones, and Truesdell (1976).

The stability relations of the iron oxides and sulfides in water were plotted as a function of Eh and pH in figure 4. Data from the leachates of the eleven wastes and a pyrite standard, equilibrated under the same

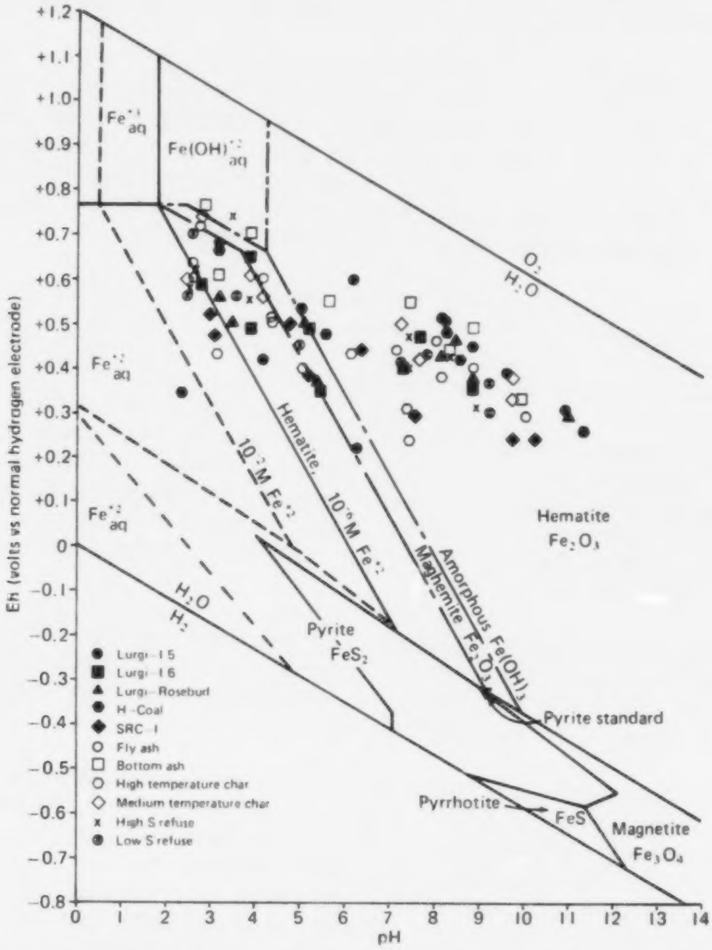

Figure 4. Stability relations of iron oxides and sulfides in waste at 25°C when $Fe^{+2}_{aq} = 10^{-6}$ M, and the sum of sulfur species is 10^{-3} M (native sulfur field excluded).

conditions as the solid wastes, were also plotted. Some explanation of figure 4 may help to interpret the data. The upper and lower limits of water stability are shown; they mark the upper and lower boudaries of the Eh and pH of concern. Thus, water decomposes into oxygen gas at Eh and pH values above the upper boudary; water decomposes into hydrogen gas at the lower boundary. Eh and pH values outside this range, therefore, are not normally of concern when interpreting the aqueous chemistry of natural systems.

The solid lines between solid phases such as hematite and magnetite mark the boundaries of mineral stabilities. Data points falling within these regions indicate that the samples are within the stability field of that particular mineral. Most of the data points in figure 4 fall within the hematite stability field. This is reasonable because x-ray diffraction showed hematite to be present in most of the samples; however, magnetite and pyrrhotite were also shown to be present in some of the solid wastes. The diagram illustrates that these two minerals are unstable in these systems and, given sufficient time, they will decompose to other mineral phases.

Data points that fall on or near a boundary line, such as the pyrite standard (fig. 4), indicate that a solution is in simultaneous equilibrium with the various solid phases described by the boundary. The pyrite used in this study was a technical grade material that contained impurities in the form of hematite and magnetite; thus it is reasonable that the solution would be in equilibrium with these three mineral phases, and that the electrodes used in the measurements were operating properly.

The boundaries between solid phases and aqueous species (such as between hematite and the aqueous Fe^{+2} ion) serve as true "solubility" boundaries; they are a function of the activity of the ion in solution. Two such boundaries are shown in figure 4—one for 10^{-6}M, and another for 10^{-2}M Fe^{+2}_{aq}. The 10^{-6}M boundary is chosen by convention, on the premise that if an ion's activity in equilibrium with a solid phase is less than 10^{-6}M, the solid will be immobile in that particular environment. This convention was developed largely from experience but seems to correlate well with natural geologic systems (Garrels and Christ, 1965). The 10^{-2}M boundary was chosen because it corresponds to the upper limit of Fe^{+2} concentrations measured in the leachates from the solid wastes.

The boundary between two aqueous species such as the Fe^{+2} and Fe^{+3} ions is drawn where the concentration of each ion is equal; thus the labeled areas are those where the particular ion is dominant, even though small concentrations of other ions may also be present.

The 10^{-6}M boundaries of the metastable minerals maghemite and freshly precipitated ferric hydroxide are drawn as broken lines. Maghemite and ferric hydroxide are unstable with respect to hematite, pyrite, and magnetite, and given sufficient time, they will convert to the thermodynamically stable minerals. However, maghemite and ferric hydroxide are clearly of more than transitory existence in natural environments and warrant consideration as mineral phases that probably control iron concentrations during the initial leaching of solid wastes, which is probably the environmentally critical period.

The data plotted in figure 4 indicate that amorphous ferric hydroxide is probably a control on iron concentrations in the leachates at pH values less than 7. Indeed, computations of ion activity products for the leachates agree with the solubility constant for the amorphous ferric hydroxide in the acid solutions. The mineral phases that were identified through chemical equilibrium modeling as contributing to the control of the ionic composition of the leachates were summarized (table 19).

Iron concentrations tended to drop below detectable levels in the alkaline solutions. These low concentrations were predicted by the solubility modeling, and they support the interpretations given in the mineral stability diagram (fig. 4).

The plot of the data in figure 4 shows that the Eh-pH relations of the alkaline leachates are not being controlled by equilibria between minerals given on the diagram. Figure 5 shows the aqueous stability relations of the manganese oxide-carbonate system. The manganese oxides and carbonates are very likely in equilibrium in the alkaline leachates, whereas the acid leachates fall in the aqueous Mn^{+2} ion field—facts that are supported by the computations of the ion activity products for the manganese minerals (table 19). These computations showed that the alkaline solutions were generally in equilibrium with the manganese oxides or carbonate on whichever boundary the particular data points shown in the diagram fell. The acid leachates were undersaturated with respect to the various manganese minerals (fig. 5). Thus, it appears that manganese oxides are controlling the Eh-pH relations of the alkaline leachates and the metastable, freshly precipitated ferric hydroxide is controlling the Eh-pH relations in the acid leachates.

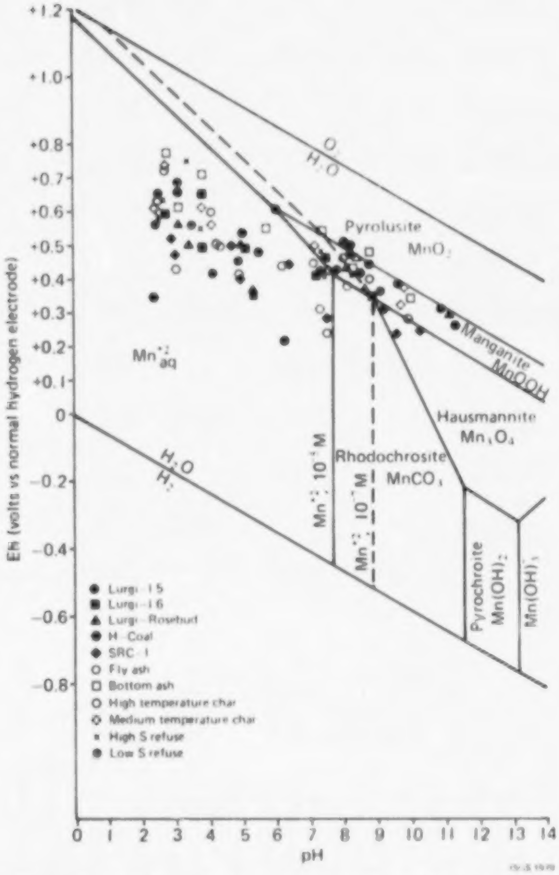

Figure 5. Stability relations of manganese oxides and carbonates in water at 25°C when total carbonate species is 10^{-3}M.

The solubilities of gypsum and anhydrite exerted a dominant influence over calcium and sulfate concentrations in the leachates at all pH levels, with the exception of the H-Coal, bottom ash, high-temperature char, and low-sulfur refuse leachates (fig. 6). Whereas these leachates were all undersaturated with respect to gypsum, gypsum still provided the upper

TABLE 19. MINERAL PHASES CONTRIBUTING TO THE CONTROL OF THE IONIC COMPOSITION OF LEACHATES FROM COAL UTILIZATION SOLID WASTES

		Lurgi Ill. #5		Lurgi Ill. #6		Lurgi-Rosebud		H-Coal		SRC		Fly ash		Bottom ash (slag)		High-temp. char		Medium-temp. char		High-sulfur refuse		Low-sulfur refuse	
Mineral	Formula	Base	Acid	Base	Acid	Base	Acid	Base	Acid	Base	Acid	Base	Acid	Base	Acid	Base	Acid	Base	Acid	Base	Acid	Base	Acid
Magnesite	$MgCO_3$					EQ		EQ		EQ				EQ									
Dolomite	$CaMg(CO_3)_2$	EQ				SS		EQ		SS		EQ		EQ								EQ	
Calcite	$CaCO_3$	EQ				EQ		SS		SS		SS		EQ		EQ		EQ		EQ		EQ	
Strontianite	$SrCO_3$	EQ		EQ		SS		EQ		SS		EQ		EQ		EQ		SS		EQ		EQ	
Rhodochrosite	$MnCO_3$	EQ				EQ				EQ		EQ		EQ		EQ		EQ				EQ	
Anhydrite	$CaSO_4$	EQ	EQ	EQ	EQ	EQ	EQ			EQ	EQ	EQ	EQ						EQ	EQ	EQ		
Gypsum	$CaSO_4 \cdot 2H_2O$	EQ	EQ	EQ	EQ	EQ	EQ		EQ	EQ	EQ	EQ	EQ					EQ	EQ	EQ	EQ		
Barite	$BaSO_4$	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ		EQ	EQ	EQ	EQ	EQ	EQ
Fluorite	CaF_2					EQ		EQ				EQ				EQ						EQ	EQ
Fluorapatite	$Ca_5(PO_4)_3F$	SS		SS		SS		SS		SS		SS		SS		SS		SS		SS		SS	
Hydroxyapatite	$Ca_5(PO_4)_3OH$	SS		EQ		EQ		SS		EQ		SS										EQ	
Strengite	$FePO_4 \cdot 2H_2O$						SS				EQ		EQ				EQ		EQ		EQ		SS
Manganese phosphate	$MnHPO_4$						EQ				EQ					EQ	EQ	EQ			EQ	EQ	EQ
Magnetite	Fe_3O_4	SS	SS	SS	SS	SS	EQ	SS	EQ	SS	EQ	SS	EQ	SS	EQ			SS	SS	SS		SS	EQ
Hematite	Fe_2O_3	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS
Maghemite	Fe_2O_3	SS	SS	SS	EQ	SS	EQ	SS	SS	SS	EQ	SS	EQ	SS	EQ	SS	SS	SS	EQ	SS	EQ	SS	SS
Goethite	FeOOH	SS	SS	SS	SS	SS	SS	SS	SS	SS	EQ	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS	SS
Amorphous $Fe(OH)_3$	$Fe(OH)_3$	SS	EQ	SS	EQ	SS	EQ	SS	EQ	SS	EQ	EQ	EQ	SS		SS	EQ	EQ	EQ	SS		EQ	
Pyrolusite	MnO_2	SS		EQ		EQ		EQ				EQ		EQ				SS		EQ		EQ	
Birnessite	MnO_2	EQ				EQ		EQ						EQ				EQ					
Nustite	MnO_2	EQ				EQ		EQ				EQ		EQ				EQ				EQ	
Bixbyite	Mn_2O_3	SS		EQ		SS		SS		EQ		SS		SS		EQ		SS		EQ		EQ	
Hausmanite	Mn_3O_4	SS		SS		SS		SS		EQ		EQ		EQ		EQ		SS				EQ	
Manganite	MnOOH	SS		EQ		SS		SS		EQ		EQ		EQ		EQ		EQ		EQ		EQ	
Amorphous $Al(OH)_3$	$Al(OH)_3$				EQ		EQ																
Diaspore	AlOOH		SS		SS		SS	EQ		EQ		SS	EQ	EQ	EQ	SS		SS	EQ	EQ	EQ	SS	
Boehmite	AlOOH		EQ		SS		SS	EQ		EQ		EQ	EQ	EQ		EQ	EQ	EQ		EQ		EQ	
Amorphous SiO_2	SiO_2	EQ	EQ	EQ	EQ	EQ	EQ				EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ		EQ	EQ	EQ
Quartz	SiO_2	EQ	SS	EQ	SS	EQ	SS		EQ	EQ	EQ	EQ	SS	EQ	SS	EQ	EQ	EQ	SS	EQ	SS	EQ	SS

EQ = Equilibrium.

SS = Supersaturation.

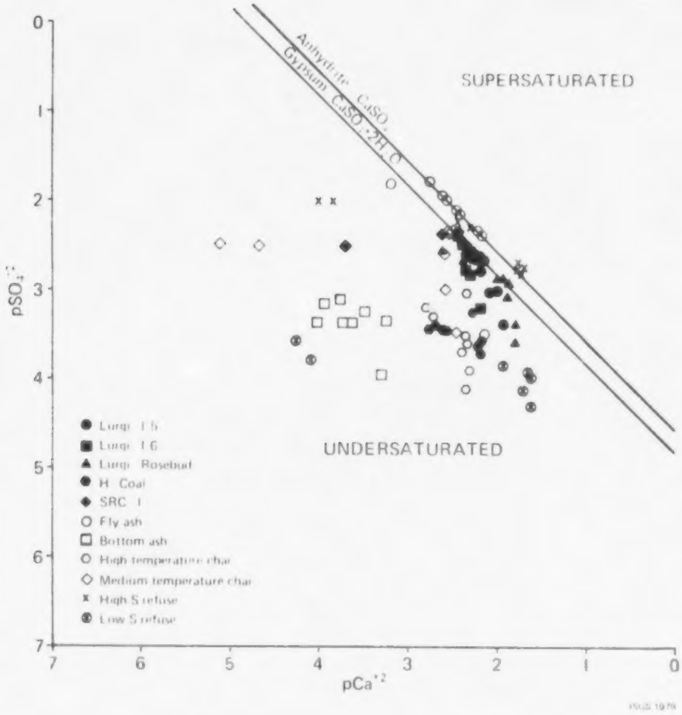

Figure 6. Calcium sulfate equilibria of leachates from coal utilization solid wastes.

boundary for prediction of calcium and sulfate concentrations. This is significant for the H-Coal residue, because it contained high concentrations of sulfur, but had low water-soluble sulfur levels, for all the sulfur species considered. This illustrates the need for information on mineral forms in the solid waste, in addition to chemical analysis of the waste.

The three Lurgi ashes, the medium-temperature char, and the SRC-I residue were generally in equilibrium with gypsum, whereas the fly ash and high-sulfur cleaning refuse were in equilibrium with anhydrite. The exceptions in these samples were those at high pH, where Ca concentrations in solution were limited by $CaCO_3$ equilibria.

The calcium carbonate equilibria of leachates from the eleven solid wastes in contact with air are shown in figure 7. Calcium concentrations in the acid leachates were usually controlled by gypsum and anhydrite equilibria; they appear as a vertical line independent of carbonate activity. Calcium concentrations in highly alkaline solutions in contact with atmospheric carbon dioxide should be controlled by calcite solubility. The data plotted in figure 7 indicate that leachates with pH values between 7.0 to 7.5 were undersaturated with respect to calcite, whereas those leachates with pH values greater than 7.5 were generally supersaturated with respect to calcite.

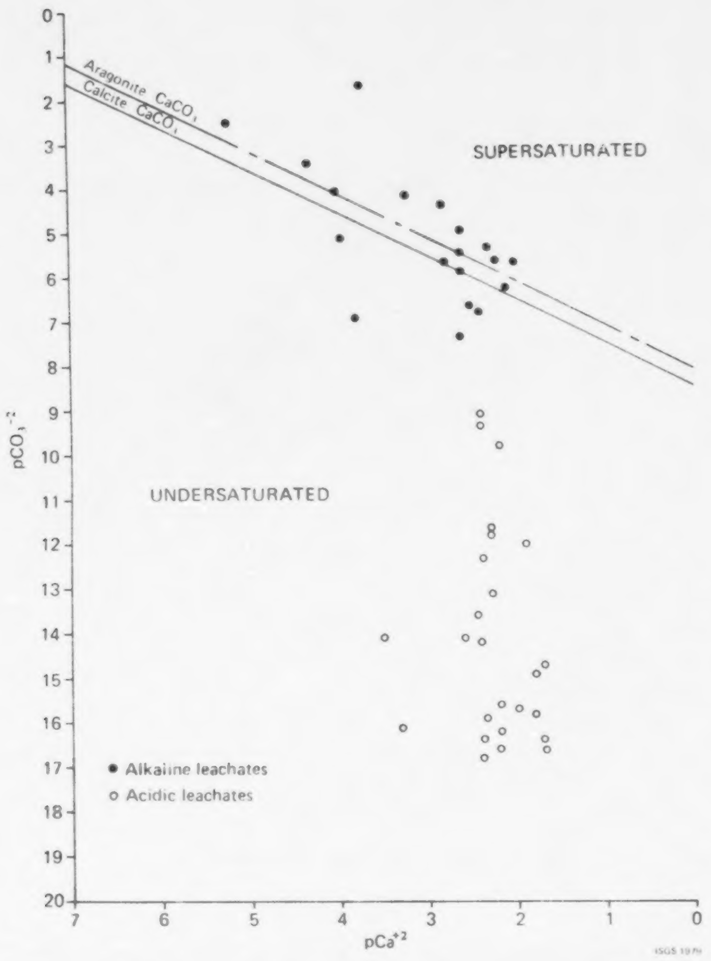

Figure 7. Calcium carbonate equilibria of leachates in contact with air from coal utilization solid wastes.

Other researchers have noted that calcite is more soluble when the Mg ion is present, which was the case in these leachates. Hassett and Jurinak (1971) found that calcites with low levels of Mg increased in solubility. Similarly, Berner (1975) showed that incorporation of Mg within the calcite crystal caused the resulting mangnesian-calcite to be considerably more soluble than pure calcite. Furthermore, Akin and Lagerwerff (1965) demonstrated that Mg and SO_4 enhanced the solubility of calcite. It seems, therefore, that the mixed-salt system occurring in these leachates yields a calcium carbonate mineral with higher solubility than either pure calcite or aragonite. Using the solubility product for pure calcium carbonate minerals to predict the calcium concentration of the alkaline leachates could result in error by underestimating the true Ca concentrations.

Figure 8 shows the silicon dioxide and aluminum hydroxide solubility equilibria. Most samples fell within the range of Si solubilities that are expected from amorphous glass and quartz. This is consistent with the

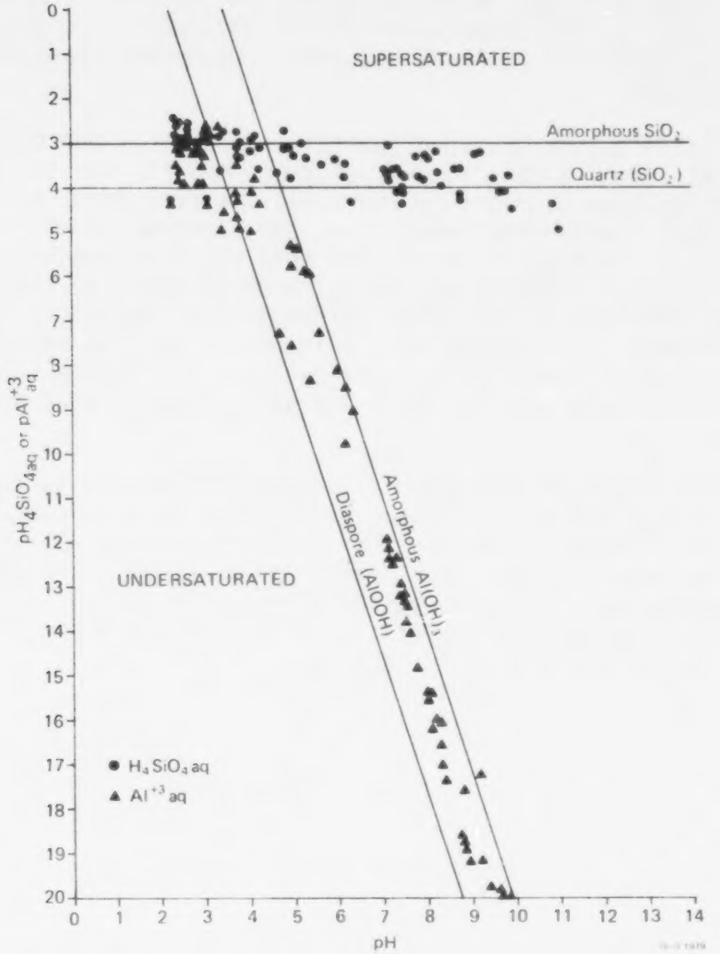

Figure 8. Silicon dioxide and aluminum hydroxide solubility equilibria of leachates from coal utilization solid wastes.

experimental design, which employed glass carboys as the equilibration vessel, and in which quartz was identified in all the solid wastes. Clearly, amorphous SiO_2 is not the most stable phase, and silica concentrations, after long periods of time, would probably be controlled by alumino-silicate minerals or quartz.

The Al equilibria, similar to the Fe and Si equilibria, were dominated in the mid-acid and alkaline pH range by the amorphous hydroxide; a metastable mineral phase was apparently controlling the solubility. These metastable mineral phases must be considered when estimating possible environmental impact during the initial leaching of coal conversion solid wastes.

The aqueous chemistry of other potential contaminants were examined (table 19); and it was found, for example, through computation of ion activity products for $BaSO_4$, that Ba concentrations in the leachates would never exceed 0.1 ppm, even in very acid solutions. Fluoride concentrations in the leachates seemed to be controlled by precipitation of fluorite (CaF_2) and fluorapatite ($Ca_5(PO_4)_3F$). Phosphate levels in the alkaline leachates would never exceed 1 ppb; this was indicated by the ion activity product calculations for fluorapatite and hydroxyapatite ($Ca_5(PO_4)_3OH$). In the acid leachates, the precipitation of iron and manganese phosphates apparently controls the phosphate levels.

The results of this study have several implications concerning heavy metals. The data suggest that removal of trace metals such as Cd, Co, Cr, Cu, Ni, Pb, and Zn from slurry pond leachates may be controlled by adsorption on or coprecipitation with iron, manganese, and aluminum oxides and hydroxides. Trace metals would continue to be removed this way for long periods of time because the adsorptive capacity of the solid phase would be continually replenished by formation of new metal oxides in the leachates. In any case, partitioning between trace metals and solid phases must be considered when evaluating trace metal mobility in these systems, and furthermore, sulfate, hydroxide, and carbonate are the major inorganic ligands that must be considered.

Thus, application of thermochemical solubility models to the coal solid waste leachates examined in this study has yielded some valuable insights into the potential these wastes have for pollution. Application of these models has shown that, whereas the concentrations of chemical constituents in the solid wastes and leachates varied over a wide range, similar mineral phases controlled the aqueous solubility of many major, minor, and trace ionic species for all of the solid wastes.

SECTION 8

SOIL ATTENUATION OF CHEMICAL CONSTITUENTS IN LEACHATES FROM COAL SOLID WASTES

INTRODUCTION

When evaluating the potential coal solid wastes have for pollution, it is important to consider where the soluble constituents of the wastes go during land disposal. Of primary importance is the characterization of the waste and waste leachate and the soil or receiving medium; these characterizations can be conducted by a number of laboratory techniques and are not difficult to determine. What is more difficult to determine, however, is the interaction that takes place when the wastes or waste leachates and soils are brought together, as in a simulated landfill condition. The problems in duplicating field conditions in the laboratory, as is well known, stem from the nonsteady state of physical parameters. To determine the long-term effects of disposal, it is also desirable to understand the physical, chemical, and biological mechanisms of constituent removal.

This investigation includes an experimental method designed to determine soil-waste interactions, plus a discussion of environmental problems that could possibly result from the disposal of coal solid wastes. Also included is a technique for the prediction of constituent migration distance. A detailed discussion of the mechanisms that remove hazardous elements from soil applied wastes has been omitted since it can be found elsewhere: in Fuller (1977), Phillips and Nathwani (1976), and Braunstein, Copenhaver, and Pfuderer (1977). We have included, however, a discussion of these removal mechanisms as they apply to the wastes analyzed in this investigation.

DISPERSED SOIL METHODOLOGY

Soils are ideal media for waste disposal because their attenuating behavior can render many of the hazardous properties harmless; then the wastes can be eventually incorporated into the soil system (Phillips and Nathwani, 1976). Before disposal, however, it is desirable to have some idea of the results of the soil-waste interaction, which will vary with wastes and soil types.

In the past, column leaching studies have determined the results of soil-waste interaction. There are two principal difficulties with column leaching studies: the long period of time required, and the difficulty in simulating field flow patterns. For example, it may require up to a year to obtain the necessary data for soils with high clay contents, and even sandy soils may require several months.

Farquhar and Rovers (1976) and Rovers, Mooij, and Farquhar (1976) designed a dispersed soil (batch reactor) methodology as an alternative technique. They conducted simultaneous experiments using dulpicate soils and wastes to examine dispersed soil and column leaching techniques. For the latter, they used both undisturbed and remolded soil samples. Their success in comparing the use of these two types of soil samples enabled them to develop the dispersed soil technique, which represents a remolded soil. Their subsequent experimentation illustrated this, but not without the following reservations and assumptions: (1) the effects of lateral dispersion cannot be measured; (2) intergranular flow must be assumed; (3) no microbial activity is assumed because of the short duration of the dispersed soil method; (4) the remolded soil column must be leached in conjunction with the batch reactors to determine the degree of attenuation caused by dilution by soil water; and (5) it is difficult to accurately predict the attenuation of contaminants that undergo retarded removal.

The first two factors are also true for column studies. The inability to measure the effects of microbial activity as an attenuation factor is a trade off for the short period of time needed for the dispersed soil experimentation. The last two factors listed above, however, are the most critical. The need for leaching a remolded soil column simultaneous to the batch reactors would result in lengthening the experimentation time. An increase in the waste solution to soil ratio in the batch reactors, however, would reduce the importance of dilution by soil water as an attenuation mechanism. Most waste leachates are highly complex systems and certain elemental components will be selectively removed prior to other elements. It is difficult to predict with any certainty the degree of attenuation of constituents that undergo retarded removal, with a technique that would not take an unreasonable amount of time.

EXPERIMENTAL DESIGN

A modified version of the dispersed soil technique developed by Farquhar and Rovers (1976) was used to determine the behavior of constituents in the aqueous supernatant solutions from the coal solid wastes.

Three sets of five 1-liter linear polyethylene bottles were used as reaction vessels (fig. 9); each set was used to study one soil. After the soils had been brought to

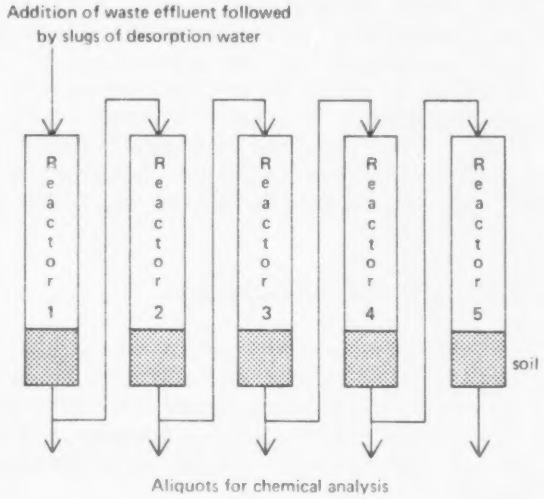
Addition of waste effluent followed by slugs of desorption water
Reactor 1
Reactor 2
Reactor 3
Reactor 4
Reactor 5
soil
Aliquots for chemical analysis

Figure 9. Schematic diagram of dispersed soil methodology.

field capacity (moisture content), 700 mL or an equivalent volume of filtered (0.45 μm Millipore) supernatant from the waste slurries were added. Then the vessels were shaken using an Equipoise^R Heavy-Duty Shaker at a rate of 265 oscillations per minute. The shaking lasted for 1½ hours, which was sufficient time to develop equilibrium conditions (Rovers, Mooij, and Farquhar, 1976). The samples were then filtered through Whatman #45 filters, and 60 mL of the filtrate was filtered again through Millipore^R .45 micron pore size membrane filters. The 60 mL portion was withdrawn for chemical analysis, and the remaining solution was transferred to the next reaction vessel in the series. A 60 mL sample was collected from each of the post-contact solutions. This procedure was repeated to determine the constituents that could be desorbed from the soils after mixing with the leachates. This was accomplished by passing distilled water through the reaction series.

Three Illinois soils—Ava silty clay loam (sicl), Bloomfield loamy sand (ls), and Catlin silt loam (sil)—with a broad range of physical and chemical characteristics, were collected and characterized (table 20). Twelve waste leachates were studied, including 10 of the 11 aerated natural (unadjusted) pH supernatant solutions. The Lurgi gasification waste using the Illinois No. 5 Coal did not possess sufficient sample volume for analysis. Also, both of the acid-aerated liquefaction leachates, H-Coal$_4$ and SRC$_4$, were studied to assess the fate of their relatively high trace metal concentrations.

The filtrates collected from this study were analyzed for 10 constituents: Al, B, Ca, Fe, K, Mg, Mn, Na, SO_4, and Zn. These constituents were chosen because they were the constituents present in the leachates in sufficient concentrations to be potential pollution hazards after being leached through soil. The filtrates collected from the two acid coal-liquefaction leachates were also analyzed for: Be, Cd, Co, Cr, Cu, F, Ni, and Pb.

ATTENUATION RESULTS

It is difficult to make broad generalizations about varied, complex systems such as the waste leachate-soil mixtures. One could say, however, that the attenuation of constituents in each leachate was similar for each soil type, although the degree of removal or elution of individual

TABLE 20. SOIL CHARACTERISTICS

Soil	pH	CEC (meq/100 g)	Surface area, N_2 (m^2/g)	Organic carbon (%)	Sand (%)	Silt (%)	Clay (%)
Catlin silt loam	7.1	18.1	10.1	4.73	11.6	60.9	27.2
Ava silty clay loam	4.5	13.1	28.3	1.18	2	69.6	28.4
Bloomfield loamy sand	5.7	0.8	1.7	0.21	82	10	8

constituents varied with soil type (table 21). Most of the constituents were attenuated through the reactor series; however, because of selective removal, some of the constituents for certain wastes were first eluted from the soils before undergoing attenuation.

To illustrate the rate of attenuation or elution, figures 10 through 16 were drawn to represent typical examples of constituent behavior. The figures depict the constituent concentration vs. the soil leachate ratio, which is the grams of soil necessary to remove or elute the indicated concentration of a constituent from one milliliter of leachate. Also included is the original supernatant concentration and a recommended water quality standard (U.S. EPA, 1972) for comparison. A figure depicting the additional trace elements (Be, Cd, Co, Cr, F, Ni, and Pb) that were determined for the two acid-aerated liquefaction wastes could not be drawn because these elements were removed to less than detectable concentrations in the first reaction vessel.

TABLE 21. SUMMARY OF SOIL-ATTENUATION BEHAVIOR OF CHEMICAL CONSTITUENTS IN LEACHATES FROM SEVERAL COAL SOLID WASTES

Elements	
Al, B, Ca, Total Fe, Na*, SO_4, Zn	Attenuated
Additional trace metals	
K*	Variable
Mg	Eluted
Mn	pH-dependent variability

*Eluted or steady at low concentrations (<10 ppm).

Iron and zinc were the two metals that were most often present in the highest concentrations in the waste leachates. Figure 10 is a plot of the zinc concentration through the leachate-soil mixtures for the natural pH leachate (pH 4.12) from the fly ash with an original zinc concentration of 20 ppm. Figure 11 is a similar diagram for total iron for the most acidic SRC liquefaction residue leachate (pH 3.5); in this case, the original total iron concentration in the leachate was 2962 ppm.

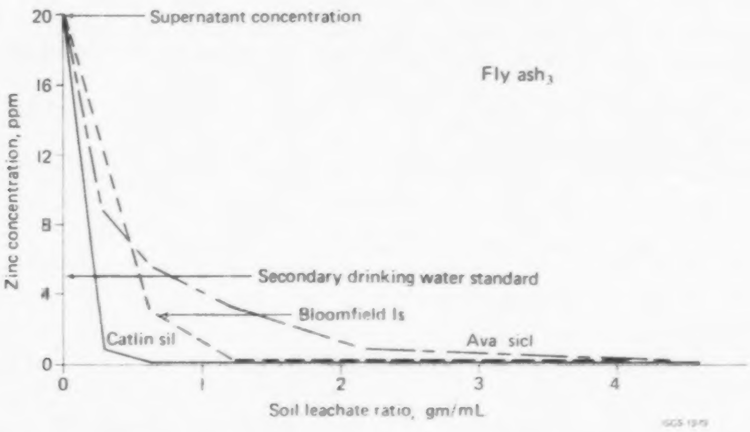

Figure 10. Zinc concentrations vs. soil/leachate ratio for fly ash$_3$ (pH 4.12).

Catlin soil proved to be the most efficient of the three soils tested in removing metals from solution. This is probably due to its higher cation-exchange capacity and its higher pH (7.1). The higher exchange capacity of the Catlin soil and its higher buffering ability enables it to neutralize acidic leachates better than the other two soils, and in many cases, precipitation of metal hydroxides will result. Probably adsorption as well as precipitation are significant for the removal of metals in cases where the metal concentrations are as high as those described above. Thus, the high clay and organic content of the Catlin soil would make it a better medium for adsorption than the other two soils. Figures 10 and 11 illustrate the "worst" cases for two metals that are found throughout the supernatant solutions. In the other leachate solutions, these metals were either present in concentrations too low for detection, or they were attenuated during mixing in the first reaction vessel to concentrations too low for detection. None of the metals mentioned above displayed any degree of elution from the soils.

Because of their selective removal, the behavior of the other constituents measured in the attenuation analysis was not as consistent or as easily interpreted as that of the metals discussed above. From this investigation, Mg and Mn emerge as having the most potential for pollution from land disposal of the coal solid wastes. Both Mg and Mn undergo various degrees of elution (negative attenuation), depending upon the particular waste leachate-soil mixture.

Figures 12 and 13 are plots of the elution of Mn through the reactor series for two of the liquefaction residue leachates. Overall, the greatest elution of Mn occurred in the liquefaction residue leachate-soil mixtures. In a typical example (fig. 12), an initial flush of Mn from the soil is followed by adsorption or reverse exchange out of solution. The trend is generally that the more acid the leachate-soil mixture, the higher the

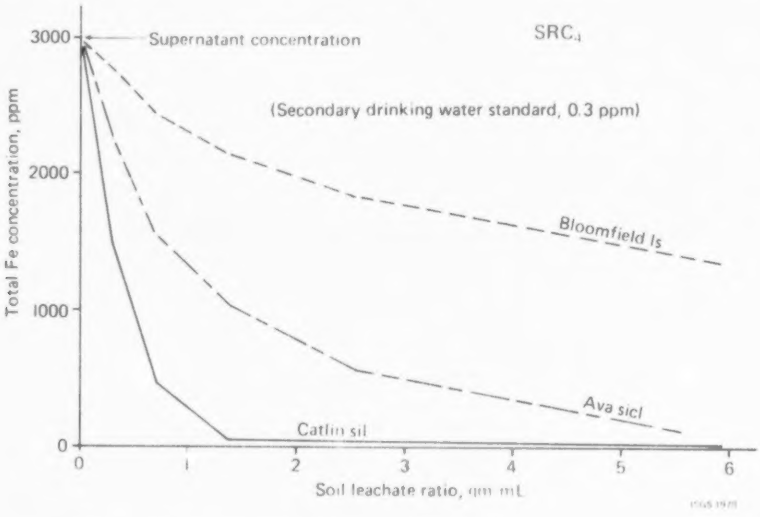

Figure 11. Total Fe concentration vs. soil/leachate ratio for SRC_4 (pH 3.5).

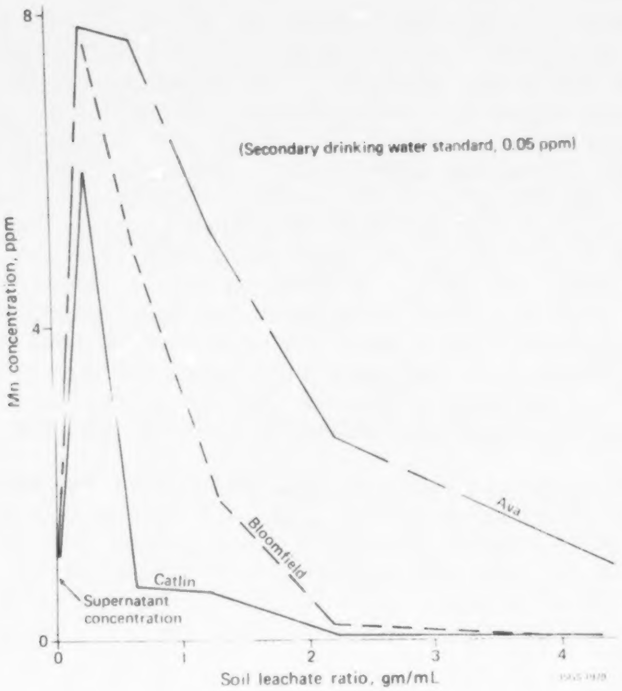

Figure 12. Manganese concentration vs. soil/leachate ratio for SRC (pH 4.69).

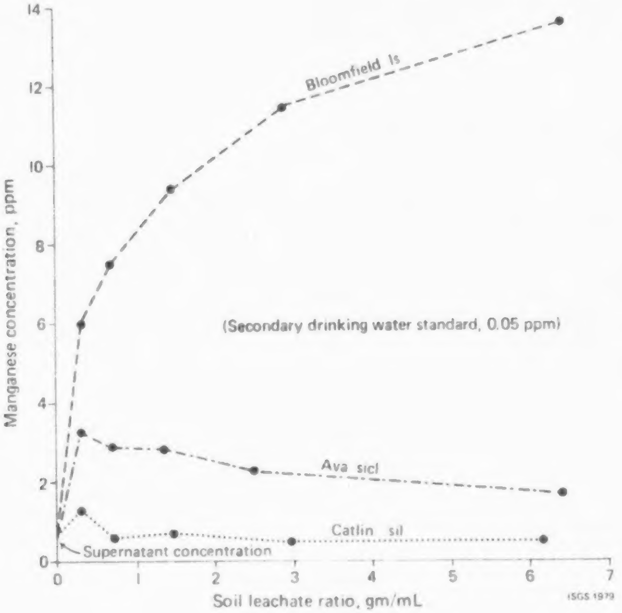

Figure 13. Manganese concentration vs. soil/leachate ratio for H-Coal (pH 3.10).

concentration of Mn initially eluted. A mixture of the acid H-Coal leachate with the Bloomfield soil, however, resulted in a greater elution of Mn than when the leachate contacted the other two soils (fig. 13). A similar example is the acid SRC_4, where the initial leachate Mn concentration is 5.4 ppm and the final Bloomfield elution was 108.2 ppm Mn. The recommended water quality level for Mn is 0.05 ppm (U.S. EPA), 1972). The other mixtures exhibit a pattern similar to that of figure 12, but the initial eluted Mn concentrations are in the range of 0.5 to 4.0 ppm.

An elution of Mg is observed for all the leachate-soil mixtures with the exception of the Bloomfield mixture (fig. 14). In several cases, the increase in Mg concentration is as high as 300 ppm. These flushes of Mg are thought to be caused by cation-exchange reaction in the soil. The flushes of minerals have been found to cause increases in the hardness of groundwaters around waste disposal sites similar to those envisioned for the disposal of coal conversion wastes (Griffin and Shimp, 1978).

The fate of boron in the coal wastes is of interest because it was found to exceed the recommended water quality levels for irrigation water in all of the waste leachates, except for the water-quenched slag. Boron's concentration ranges from 5 ppm to as high as 65 ppm (Lurgi Ash, Rosebud Seam Coal) in the leachates. Catlin soil, followed by Ava and Bloomfield respectively, was the most efficient at removing boron (fig. 15). Other researchers have shown that boron is readily adsorbed by illite (Harder, 1961; and Couch and Grim, 1968), and that adsorption increases with increasing pH (Sims and Bingham, 1967). Both of these factors favor higher retention of boron by Catlin soil than the Ava and Bloomfield soils.

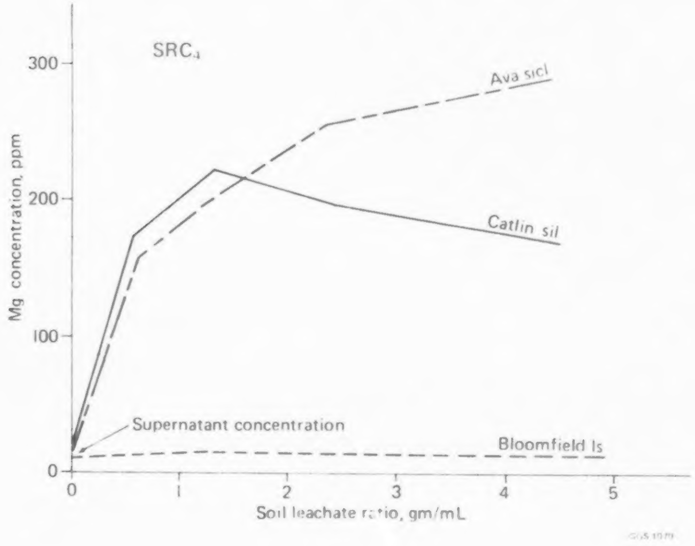

Figure 14. Mg concentration vs. soil/leachate ratio for SRC (pH 3.5).

In almost all of the natural pH supernatant solutions, calcium and sulfate are the dominant cation and anion in solution. Over the pH range studied, SO_4^{-2} is the dominant sulfur species in solution (Garrels and Christ, 1965; Stumm and Morgan, 1970). Because of the high concentrations of both calcium and sulfate and the rate at which they are removed from solution, the precipitation of gypsum ($CaSO_4 \cdot 2H_2O$) and/or anhydrite ($CaSO_4$) would seem to be an important attenuation mechanism. Figure 16 plots the typical case for sulfate attenuation with the trend of Ava > Catlin > Bloomfield. Adsorption of sulfate could also be occurring with the acid leachate-Ava mixture, although, because of the amount of sulfate being removed (Bolt and Bruggenwert, 1976), it is unlikely that this is the only mechanism.

Figures 17 and 18 are combined plots of calcium and sulfate behavior through the reactor series. The figures have been normalized by using C/Co (the constituent concentration in each reaction vessel/the original leachate concentration) for the vertical axis. The first plot indicates there is a definite relationship between the removal of calcium and sulfate, which supports an interpretation that precipitation of gypsum is the dominant attenuation mechanism. The second graph, however, gives the more normal case where both constituents are removed similarly in the Ava mixtures, but calcium is at least initially eluted, whereas sulfate is attenuated for the Catlin and Bloomfield mixtures. These samples indicate that in some situations, adsorption of sulfate by soil appears to be the dominant attenuation mechanism. It is difficult to account for precipitation of $CaSO_4$ for the last two leachate-soil mixtures because it was impossible to account for the available Ca from the soils themselves.

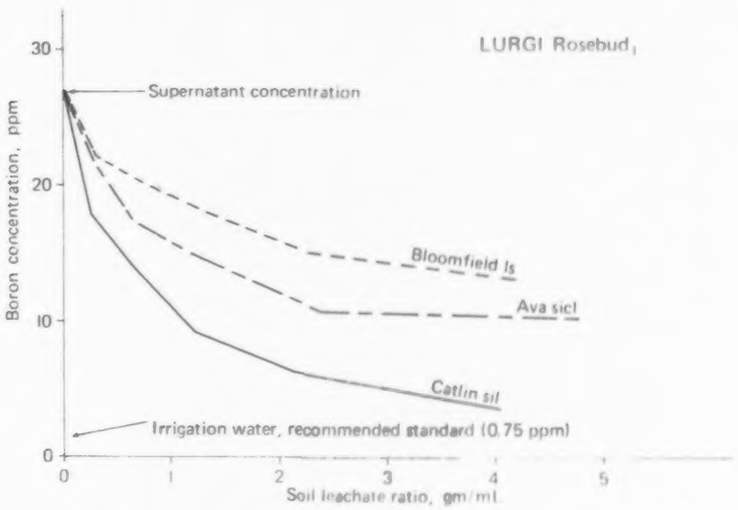

Figure 15. Boron concentration vs. soil/leachate ratio for Lurgi-Rosebud (pH 8.4).

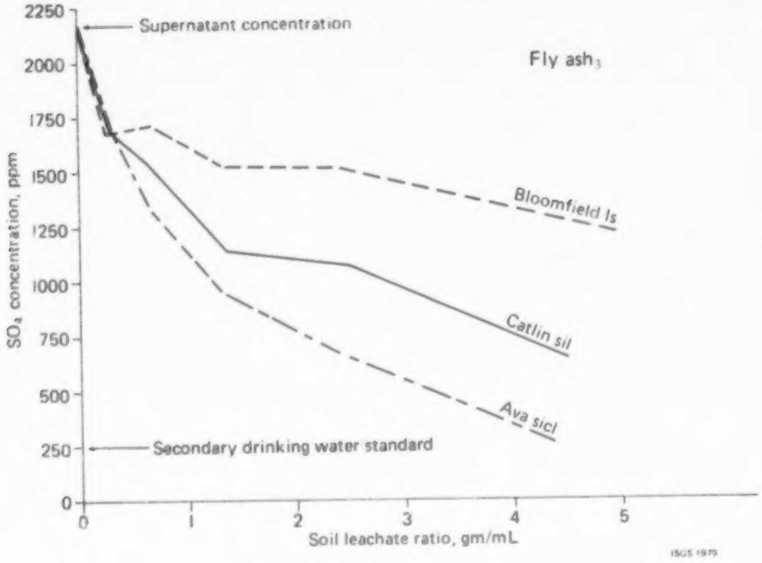

Figure 16. Sulfate concentration vs. soil/leachate ratio for fly ash (pH 4.12).

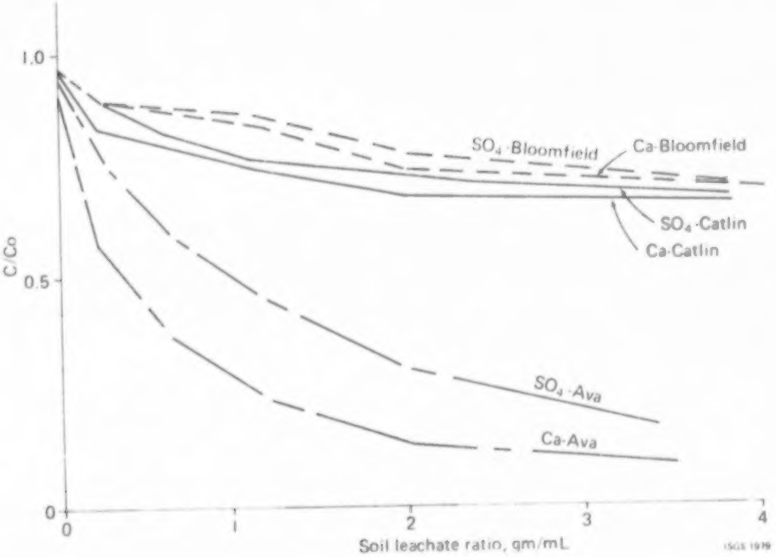

Figure 17. Ratio of concentration of Ca or SO_4 in leachate after reaction with soil to the initial concentration vs. soil/leachate ratio.

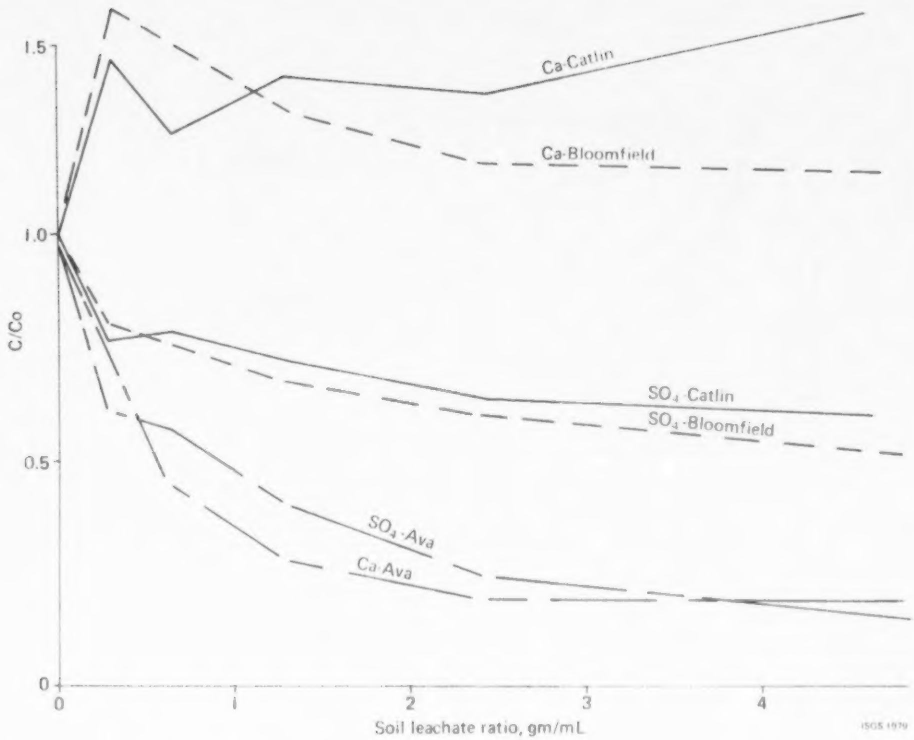

Figure 18. Ratio of concentration of Ca or SO_4 in leachate after reaction with soil to the initial concentration vs. soil/leachate ratio.

The desorption phase of the analysis resulted in two conclusions: (1) the metals which were removed rapidly during the sorption phase were not eluted from the soils during the desorption phase; and (2) as a general rule, the exchangeable cations and sulfate were brought back into solution, but not to their original leachate concentration.

CALCULATION OF MIGRATION DISTANCE

By using the dispersed soil technique, it is possible to determine how far a potential pollutant will migrate with time. By using figure 10 (the plot of the zinc concentration vs. the soil/leachate ratio for the fly ash leachate [pH 4.1]) as an example, it can be shown how to determine this migration distance.

The first step is to determine graphically the soil/leachate ratio needed to obtain the desired water quality level for the element of interest; in this case, the drinking water standard for zinc is used—5.0 ppm. For the Ava soil, the ratio equals 0.75 gm/mL. This means that for each mL of leachate, 0.75 gm of soil were needed to reduce the initial zinc concentration of the leachate down to the drinking water standard. Then it is necessary to determine the volume of leachate to be generated by the waste per unit time and the soil bulk density. From this data, the migration distance per unit time can be computed.

If it is assumed that: soil bulk density = 1.50 gm/cm^3, leachate volume = 6 in./yr (15.24 mL/cm^2 yr), and landfill life = 30 years, then the migration distance is computed to be:

$$\frac{(0.75\ \text{gm/mL}(15.24\ \text{mL/cm}^2\ \text{yr})(30\ \text{years})}{1.50\ \text{gm/cm}^3} = 228\ \text{cm or } 7.5\ \text{ft in } 30\ \text{years}$$

This calculation does not account for dilution by soil water or waters of infiltration, and interactions occurring in the soil profile prior to the subsequent waste additions reaching the leachate front.

SECTION 9

BIOASSAYS OF LEACHATES FROM COAL SOLID WASTES

INTRODUCTION

The environmental data acquisition for a complete environmental assessment of coal-based energy technology includes physical, chemical, and biological analyses (Hangebrauck, 1978). The preceding sections have comprised the physical and chemical analyses of this investigation; this section comprises the biological analysis investigation of the potential pollution hazard of coal solid wastes.

If coal conversion processes are developed on a commercial scale, they will generate an enormous amount of solid waste (Braunstein, Copenhaver, and Pfuderer, 1977). The solid wastes from coal conversion plants will probably be deposited in landfills and ponds (Talty, 1978). Landfills are subject to leaching; ponds could be contaminated and thus serve as potential sources of pollution to other water resources such as groundwater and nearby streams. Since the impact of coal solid wastes on aquatic biota has not been adequately assessed, toxicity tests of the leachates generated from these wastes were conducted with fathead minnow fry (*Pimephales promelas*).

The purposes of toxicity tests were to determine: (1) if the leachates from three Lurgi gasification ashes, an H-Coal liquefaction residue, an SRC liquefaction residue, two chars, a fly ash, a water-quenched slag, and two gob samples were acutely toxic to young fathead minnows; (2) how much dilution was necessary to eliminate mortality caused by toxic leachates on a short-term basis; (3) if the acute toxicity of leachates equilibrated under anaerobic conditions differed significantly from similar leachates equilibrated under aerobic conditions; and (4) which water-soluble constituents leached from these coal solid wastes were responsible for the toxicity.

MATERIALS AND METHODS USED FOR BIOASSAYS

Ninety-six hour static bioassays of the leachates were conducted with 1- to 6-day-old fathead minnow fry, *Pimephales promelas*. The fish were propagated in the laboratory and in outdoor ponds at the Illinois Natural History Survey in Urbana, Illinois. The leachates were obtained from the same vessels used in the solubility and attenuation studies; they were filtered through a 0.45 µm pore size membrane filter prior to the bioassays.

The toxicity tests were divided into two phases: the screening procedure and the LC-50 determination. During the screening procedure, the young fathead minnows were exposed to the "full-strength" leachates. During the LC-50 determinations, the minnows were exposed to "full-strength" leachates diluted with soft reconstituted water that was prepared according to suggestions in "Methods for Acute Toxicity Tests with Fish, Macro-invertebrates and Amphibians" (Committee on Methods for Toxicity Tests with Aquatic Organisms, 1975). The screening procedure enabled us to determine LC-50 values more efficiently, since LC-50 determinations were not needed for leachates that did not cause 50 percent mortality in the screening procedure. Procedures outlined in Litchfield and Wilcoxon (1949) were used for the LC-50 determinations.

Ten young fathead minnows were placed into glass fingerbowls (115 x 45 mm) containing 200 mL of "full-strength" or diluted leachate. Each bioassay was replicated. Fish mortality data were collected at 24, 48, 72, and 96 hours after the bioassays were begun. The test organisms were not fed and the solutions were not aerated during the bioassays. Since one-half of the leachates were equilibrated under anaerobic conditions, all solutions were aerated before the fish were added. The bioassays were conducted at a constant temperature (21 ± 1°C) and with a constant photo-period (16L-8D) in an environmental chamber. At the beginning and end of all bioassays, pH and dissolved oxygen were measured with a Beckman pH meter and a YSI dissolved oxygen meter. Specific conductance was measured at the beginning of each bioassay with a YSI portable conductivity meter.

RESULTS OF BIOASSAY STUDY

The screening procedures were conducted to determine if the "full-strength" leachates were acutely toxic. To test the effect of pH on the mortality of fathead minnows, bioassays were conducted utilizing buffered reconstituted water ranging in pH from 4.9 to 11.0. The results of the pH experiment were similar to those of the screening procedures (figs. 19 to 23). Many of the leachates and the reconstituted water were not acutely toxic to young fathead minnows if the pH of the solutions was between 6.2 and 9.0. Low mortality (5 to 20 percent) occurred, however, in 37.5 percent of the neutral leachates, and mortality was greater than 20 percent in a Lurgi Ash (Ill-5-6, pH = 7.1), H-Coal (HC-5, pH = 8.8), solvent-refined coal (SRC-6, pH = 7.3), and a low-sulfur gob (LSR-2, pH = 6.9). Total mortality occurred in those solutions with pH values less than 6.0, and mortality was 50 percent or higher in solutions with pH values greater than 10.0.

The mortalities that occurred during the screening procedures of the natural pH leachates are listed in table 22. The natural pH leachates from the Lurgi gasification process were not acutely toxic. The aerobic natural pH leachate generated from H-Coal liquefaction residue was relatively nontoxic on a short-term basis; however, HC-5, the natural pH leachate equilibrated under anaerobic conditions, was relatively alkaline (pH = 8.8), and 35 percent mortality occurred. Total mortality occurred in the aerobic natural pH leachate from SRC dry mineral residue; this leachate was acidic (pH = 5.6). The natural pH leachate of SRC equilibrated under anaerobic conditions (SRC-6) was a neutral solution (pH = 7.1); however, 40 percent mortality occurred during the screening procedure. The natural pH leachates

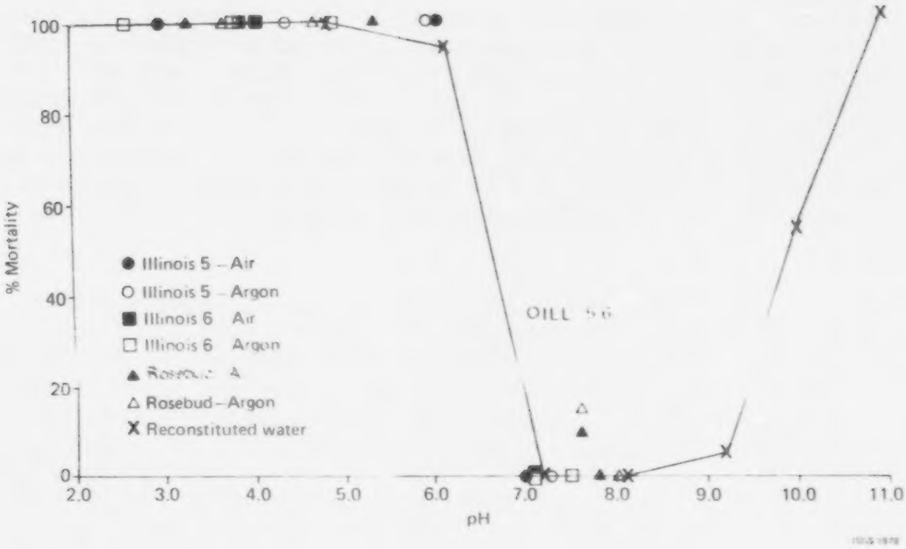

Figure 19. Percentages of mortality of 1- to 6-day-old fathead minnow fry (*Pimephales promelas*) resulting from 96-hour exposures to 24 leachates of different pHs generated from three Lurgi gasification ashes and 7 buffered solutions of reconstituted water.

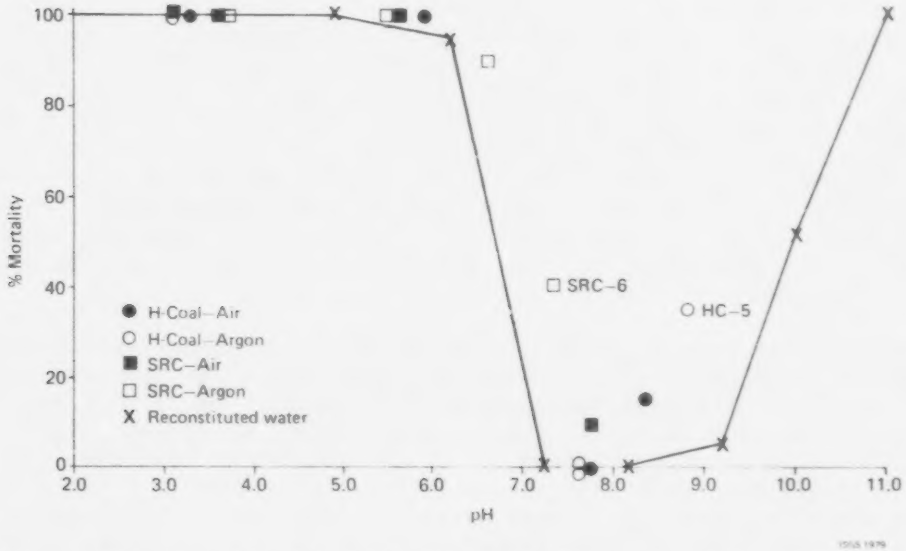

Figure 20. Percentages of mortality of 1- to 6-day-old fathead minnow fry (*Pimephales promelas*) resulting from 96-hour exposures to 16 leachates of different pHs generated from SRC and H-Coal liquefaction residue and 7 buffered solutions of reconstituted water.

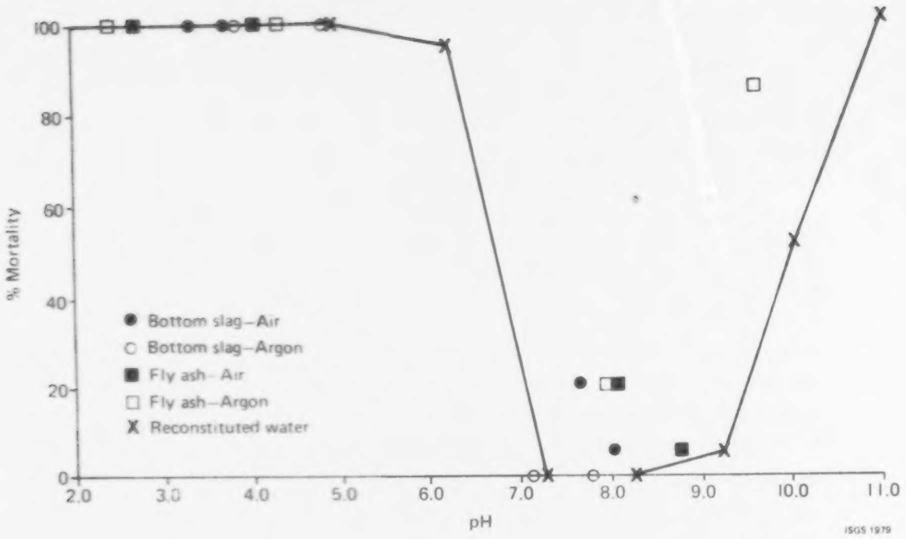

Figure 21. Percentages of mortality of 1- to 6-day-old fathead minnow fry (*Pimephales promelas*) resulting from 96-hour exposures to 16 leachates of different pHs generated from a water-quenched slag and a fly ash and 7 buffered solutions of reconstituted water.

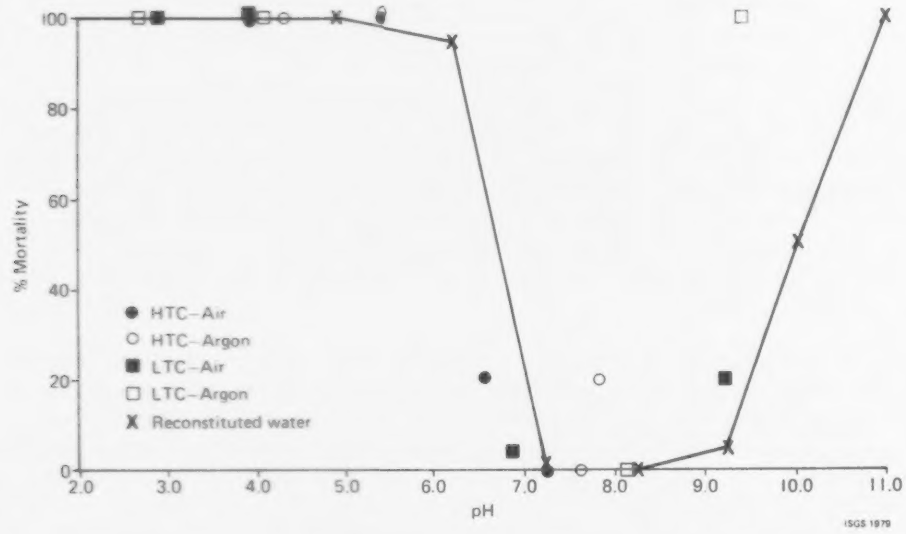

Figure 22. Percentages of mortality of 1- to 6-day-old fathead minnow fry (*Pimephales promelas*) resulting from 96-hour exposures to 16 leachates of different pHs generated from high- and low-temperature chars and 7 buffered solutions of reconstituted water.

TABLE 22. PERCENTAGES OF MORTALITY OF 1-TO-6-DAY-OLD FATHEAD MINNOW FRY (PIMEPHALES PROMELAS) RESULTING FROM 96-HOUR EXPOSURES TO THE NATURAL pH LEACHATES OF 11 COAL SOLID WASTES

Sample	Type	Atmosphere	pH	Mortality (%)
BS-1	Gasification ash	Aerobic	7.8	0
BS-5	Gasification ash	Anaerobic	8.0	0
ILL-5-1	Gasification ash	Aerobic	7.1	0
ILL-5-5	Gasification ash	Anerobic	7.3	0
ILL-6-1	Gasification ash	Aerobic	7.1	0
ILL-6-5	Gasification ash	Anaerobic	7.5	0
HC-1	Liquefaction residue	Aerobic	8.3	15
HC-5	Liquefaction residue	Anaerobic	8.8	100
SRC-2	Liquefaction residue	Aerobic	5.6	100
SRC-6	Liquefaction residue	Anaerobic	7.3	40
KS-3	Water-quenched slag	Aerobic	3.7	100
KS-7	Water-quenched slag	Anaerobic	5.8	100
FA-3	Fly ash	Aerobic	4.0	100
FA-7	Fly ash	Anaerobic	4.3	100
HSR-2	High-sulfur gob	Aerobic	7.7	5
HSR-6	High-sulfur gob	Anaerobic	8.0	0
LSR-1	Low-sulfur gob	Aerobic	8.8	15
LSR-5	Low-sulfur gob	Anaerobic	8.9	15
HTC-1	High-temperature char	Aerobic	7.2	0
HTC-5	High-temperature char	Anaerobic	7.6	0
LTC-2	Low-temperature char	Aerobic	6.8	5
LTC-6	Low-temperature char	Anaerobic	8.1	0

from the water-quenched slag and the fly ash from a coal-fired power plant were acidic (pH <5.8), and total mortality occurred in all four leachates. Low mortality (<5 percent) occurred in the natural pH leachates generated from the high-sulfur gob. Both natural pH leachates generated from the low-sulfur gob were relatively alkaline (pH values of 8.8 and 8.9), and low mortality (15 percent) occurred in these solutions. Low mortality (<5 percent) occurred in natural pH leachates generated from the high- and low-temperature chars.

Attempts were made to decrease the mortality rate caused by low pH by neutralizing some of the acidic leachate solutions with sodium hydroxide. Total mortality occurred in all neutralized solutions. Since all the neutralized solutions had specific conductance values greater than 7.00 mmhos/cm, it was postulated that the exposures to relatively large total ion concentrations resulted in "ionic shock." To test this hypothesis, several solutions of reconstituted water of differing specific conductances were prepared using NaCl; the results of 96-hour static bioassays of these solutions are shown in figure 24. Total mortality occurred in solutions with a specific conductance

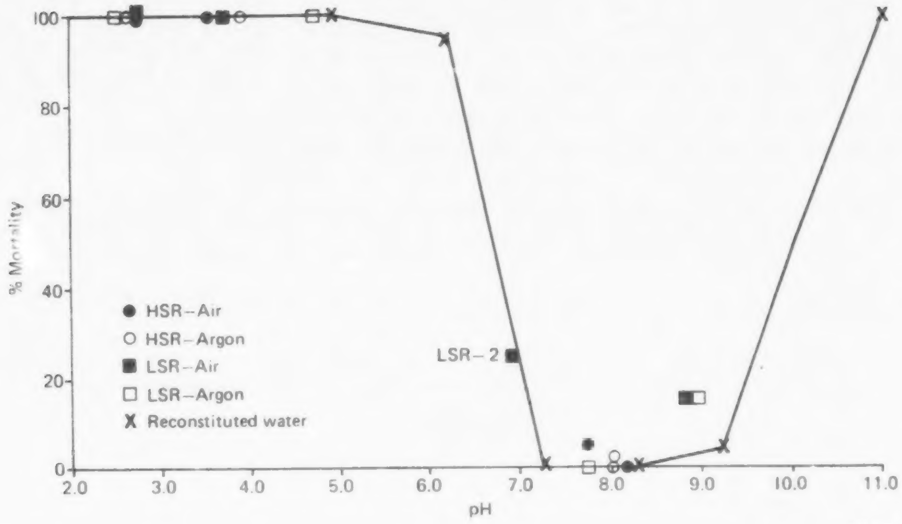

Figure 23. Percentages of mortality of 1- to 6-day-old fathead minnow fry (*Pimephales promelas*) resulting from 96-hour exposures to 16 leachates of different pHs generated from a high-sulfur gob sample and a low-sulfur gob sample and 7 buffered solutions of reconstituted water.

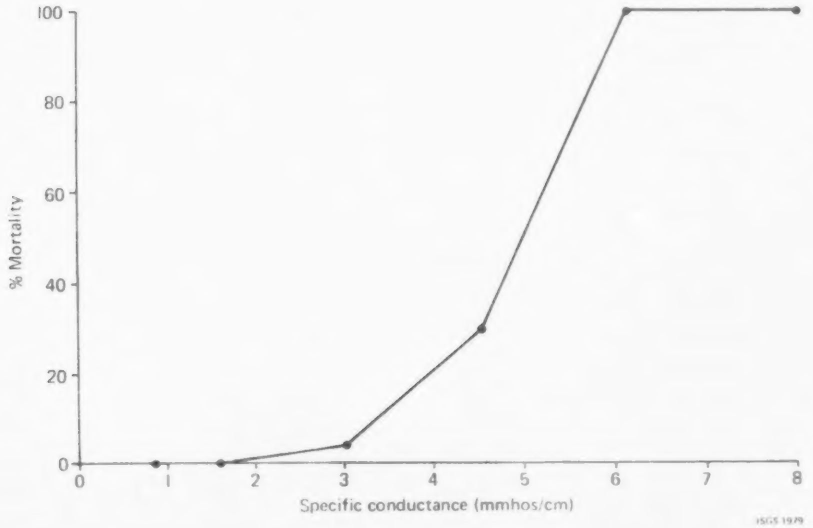

Figure 24. Percentages of mortality of 1- to 6-day-old fathead minnow fry (*Pimephales promelas*) resulting from 96-hour exposures to 7 buffered solutions of reconstituted water of different specific conductances adjusted with NaCl.

greater than 6.10 mmhos/cm. The high total ion concentrations were probably responsible for the total mortality that occurred in the neutralized acidic leachates.

The LC-50 values were determined to investigate the relative toxicities of the leachates and how much dilution was necessary to ensure their survival during 96-hour static bioassays. The LC-50 values, their 95 percent confidence intervals, and the dilutions necessary to ensure survival of the minnows are listed in tables 23 to 27. The pH values listed are those of the "full-strength" leachates after aeration and prior to dilution with reconstituted water. The

TABLE 23. THE LC-50 VALUES, THEIR 95 PERCENT CONFIDENCE INTERVALS, AND THE AMOUNT OF DILUTION NECESSARY TO ELIMINATE MORTALITY FOR THREE LURGI GASIFICATION ASH LEACHATES OBTAINED IN 96-HOUR STATIC BIOASSAYS USING 1-TO-6-DAY-OLD FATHEAD MINNOW FRY (*PIMEPHALES PROMELAS*).

Sample	Atmosphere	pH	LC-50 (mL/100 mL)	Dilution for 0% mortality
		Rosebud		
1*	Aerobic	7.8	>100	1:1
2	Aerobic	7.6	>100	1:1
3	Aerobic	5.4	18.00 ± 2.70	1:100
4	Aerobic	3.3	0.50 ± 0.13	1:769
5*	Anaerobic	8.0	>100	1:1
6	Anaerobic	7.6	>100	1:1
7	Anaerobic	4.7	2.10 ± 0.76	1:200
8	Anaerobic	3.7	0.78 ± 0.16	1:250
		Illinois No. 5		
1*	Aerobic	7.1	>100	1:1
2	Aerobic	7.0	>100	1:1
3	Aerobic	6.1	11.00 ± 3.85	1:50
4	Aerobic	3.0	1.80 ± 0.61	1:166
5*	Anaerobic	7.3	>100	1:1
6	Anaerobic	7.1	>100	1:1
7	Anaerobic	6.0	40.00 ± 16.40	1:50
8	Anaerobic	4.4	1.00 ± 0.09	1:200
		Illinois No. 6		
1*	Aerobic	7.1	>100	1:1
2	Aerobic	4.1	8.60 ± 2.92	1:43
3	Aerobic	3.9	5.20 ± 0.99	1:38
4	Aerobic	2.6	6.40 ± 0.90	1:1000
5*	Anaerobic	7.5	>100	1:1
6	Anaerobic	7.1	>100	1:1
7	Anaerobic	4.9	10.00 ± 2.60	1:26
8	Anaerobic	3.8	0.38 ± 0.01	1:1000

*Natural pH solutions

LC-50 value is the statistically determined concentration of leachate at which 50 percent mortality occurs. There is an inverse relationship between toxicity and the LC-50 value; for example, the LC-50 values for Rosebud-3 (BS_3) and BS_4 are 18.00 and 0.50, respectively (table 23). Eighteen milliliters of BS_3 diluted with 82 mL of reconstituted water was as toxic as 0.50 mL of BS_4 diluted with 99.5 mL of reconstituted water. Leachates exhibiting greater toxicity, therefore, have lower LC-50 values than less toxic leachates. If, in the "full-strength" leachates, less than 50 percent mortality occurred, the LC-50 is reported as greater than 100 mL/100 mL.

Generally, all leachates were acutely toxic when acidic (pH <6.2). With increasing acidity, toxicity also increased and the LC-50 value decreased. The LC-50 values of leachates equilibrated under aerobic atmospheres were not significantly different from LC-50 values of similar leachates equilibrated under anaerobic atmospheres (p >.05, paired t-test).

Natural pH leachates generated from Lurgi gasification ashes were not acutely toxic; therefore, their LC-50 values were greater than 100 mL/100 mL, and no dilution was necessary to achieve 0 percent mortality (table 23).

TABLE 24. LC-50 VALUES, THEIR 95 PERCENT CONFIDENCE INTERVALS, AND THE AMOUNT OF DILUTION NECESSARY TO ELIMINATE MORTALITY FOR H-COAL AND SRC LIQUEFACTION LEACHATES OBTAINED IN 96-HOUR STATIC BIOASSAYS USING 1-TO-6-DAY-OLD FATHEAD MINNOW FRY *(PIMEPHALES PROMELAS)*.

Sample	Atmosphere	pH	LC-50 (mL/100 mL)	Dilution for 0% mortality
		H-Coal		
1*	Aerobic	8.3	>100	1:1
2	Aerobic	7.7	>100	1:1
3	Aerobic	5.9	39.00 ± 4.80	1:5
4	Aerobic	3.3	29.50 ± 8.85	1:21
5*	Anaerobic	8.8	>100	1:6
6	Anaerobic	7.6	>100	1:1
7	Anaerobic	7.6	>100	1:1
8	Anaerobic	3.1	7.90 ± 1.66	1:46
		SRC-I		
1	Aerobic	7.7	>100	1:1
2*	Aerobic	5.6	21.00 ± 3.36	1:10
3	Aerobic	3.6	16.00 ± 2.72	1:10
4	Aerobic	3.1	0.36 ± 0.10	1:1000
5	Anaerobic	6.6	74.00 ± 6.22	1:2
6*	Anaerobic	7.3	>100	1:1
7	Anaerobic	5.5	25.00 ± 2.75	1:7
8	Anaerobic	3.7	0.26 ± 0.07	1:2000

*Natural pH solutions

TABLE 25. LC-50 VALUES, THEIR 95 PERCENT CONFIDENCE INTERVALS, AND THE AMOUNT OF DILUTION NECESSARY TO ELIMINATE MORTALITY FOR LEACHATES GENERATED FROM BOTTOM SLAG AND FLY ASH OBTAINED IN 96-HOUR STATIC BIOASSAYS USING 1-TO-6-DAY-OLD FATHEAD MINNOW FRY (*PIMEPHALES PROMELAS*).

Sample	Atmosphere	pH	LC-50 (mL/100 mL)	Dilution for 0% mortality
			Slag	
1	Aerobic	8.0	>100	1:1
2	Aerobic	7.6	>100	1:1
3*	Aerobic	3.7	22.50 ± 4.28	1:28
4	Aerobic	3.3	8.00 ± 1.68	1:20
5	Anaerobic	7.7	>100	1:1
6	Anaerobic	7.1	>100	1:1
7*	Anaerobic	5.8	37.00 ± 3.89	1:5
8	Anaerobic	3.8	3.90 ± 0.55	1:100
			Fly ash	
1	Aerobic	8.7	>100	1:1
2	Aerobic	8.0	>100	1:1
3*	Aerobic	4.0	9.00 ± 2.70	1:100
4	Aerobic	2.7	0.64 ± 0.08	1:2000
5	Anaerobic	9.6	80.00 ± 7.20	1:3
6	Anaerobic	7.9	>100	1:1
7*	Anaerobic	4.3	3.15 ± 0.72	1:1000
8	Anaerobic	2.4	0.68 ± 0.12	1:333

*Natural pH solutions

The aerobic natural pH leachate generated from H-Coal liquefaction residue was not acutely toxic and therefore required no dilution for 0 percent mortality. During the screening procedure, total mortality occurred in the anaerobic natural pH H-Coal leachate (table 22). During the LC-50 determination, however, 40 percent mortality occurred in the full-strength leachate, and 30 percent mortality occurred in a solution of 180 mL of HC-5 and 20 mL of reconstituted water. The LC-50 determination was made 9 months after the screening procedure was performed, and apparently the leachate had not reached equilibrium at the time of the screening procedure. The LC-50 value for HC-5, therefore, was greater than 100 mL/100 mL, even though total mortality occurred during the screening procedure (table 24). The aerobic natural pH leachate generated from the SRC liquefaction residue had a pH of 5.6, was acutely toxic, and required a 1:10 dilution to eliminate mortality. In addition, we estimate that 50 percent mortality would occur in a solution of 21 mL SRC-2 and 79 mL reconstituted water (table 24). The anaerobic natural pH SRC leachate had an LC-50 value greater than 100 mL/100 mL, and required less than a 1:1.5 dilution to eliminate mortality.

The natural pH leachate generated from the water-quenched slag and equilibrated under aerobic conditions was relatively toxic (LC-50 = 22.50 ± 4.28) and required a moderate amount of dilution (1:28) to negate its toxicity. The

TABLE 26. LC-50 VALUES, THEIR 95 PERCENT CONFIDENCE INTERVALS, AND THE AMOUNT OF DILUTION NECESSARY TO ELIMINATE MORTALITY FOR HIGH-SULFUR AND LOW-SULFUR GOB LEACHATES OBTAINED DURING 96-HOUR STATIC BIOASSAYS USING 1-TO-6-DAY-OLD FATHEAD MINNOW FRY *(PIMEPHALES PROMELAS)*.

Sample	Atmosphere	pH	LC-50 (mL/100 mL)	Dilution for 0% mortality
		LSR		
1*	Aerobic	8.8	>100	1:1
2	Aerobic	7.9	>100	1:1
3	Aerobic	5.4	57.00 ± 2.28	1:3
4	Aerobic	3.8	3.80 ± 0.41	1:50
5*	Anaerobic	8.9	>100	1:1
6	Anaerobic	7.7	>100	1:1
7	Anaerobic	6.6	96.00 ± 0.83	1:1
8	Anaerobic	4.0	2.15 ± 0.16	1:100
		HSR		
1	Aerobic	8.1	>100	1:1
2*	Aerobic	7.7	>100	1:1
3	Aerobic	3.5	41.00 ± 2.87	1:4
4	Aerobic	2.7	3.00 ± 0.62	1:67
5	Anaerobic	8.0	>100	1:1
6*	Anaerobic	8.0	>100	1:1
7	Anaerobic	3.9	56.00 ± 2.52	1:2
8	Anaerobic	2.6	2.30 ± 0.14	1:67

*Natural pH solutions

natural pH slag leachate equilibrated under anaerobic conditions was less toxic (LC-50 = 37.00 ± 3.89) and less acidic than the aerobic leachate. Both natural pH leachates generated from the fly ash were relatively toxic (LC-50 <11.70) and required a dilution of 1:100 or greater to ensure survival during the bioassay. The natural pH leachates of the two gob and two char samples were not sufficiently toxic on a short-term basis to establish LC-50 values and required little dilution (<1:1.5) to eliminate mortality (tables 26 and 27).

DISCUSSION OF BIOASSAY RESULTS

The potential hazard that coal solid wastes pose to the aquatic environment lies in the relatively large concentrations of accessory elements in the waste and the possibility of acid formation. Accessory elements could be leached from the solid wastes by water in a slag pond or water percolating through a landfill. Pyritic minerals in these solid wastes produce acid when exposed to air and water, and acid could lower the pH of the pond or the pH of the water passing through a landfill. Lowering the pH could increase the leaching of potentially hazardous chemical constituents or directly harm organisms in the affected area.

TABLE 27. LC-50 VALUES, THEIR 95 PERCENT CONFIDENCE INTERVALS, AND THE AMOUNT OF DILUTION NECESSARY TO ELIMINATE MORTALITY FOR HIGH-TEMPERATURE AND LOW-TEMPERATURE CHAR LEACHATES OBTAINED DURING 96-HOUR STATIC BIOASSAYS USING 1-TO-6-DAY-OLD FATHEAD MINNOW FRY *(PIMEPHALES PROMELAS)*.

Sample	Atmosphere	pH	LC-50 (mL/100 mL)	Dilution for 0% mortality
		LTC		
1	Aerobic	9.2	>100	1:1
2*	Aerobic	6.8	>100	1:1
3	Aerobic	4.2	12.00 ± 1.30	1:20
4	Aerobic	4.0	3.48 ± 0.48	1:50
5	Anaerobic	8.8	98.00 ± 2.00	1:1
6*	Anaerobic	8.1	>100	1:1
7	Anaerobic	4.6	17.40 ± 1.22	1:8
8	Anaerobic	3.8	1.03 ± 0.11	1:200
		HTC		
1*	Aerobic	7.2	>100	1:1
2	Aerobic	6.5	>100	1:1
3	Aerobic	5.4	5.40 ± 0.92	1:100
4	Aerobic	3.9	0.80 ± 0.18	1:333
5*	Anaerobic	7.6	>100	1:1
6	Anaerobic	7.8	>100	1:1
7	Anaerobic	5.4	14.00 ± 1.54	1:13
8	Anaerobic	4.3	3.20 ± 0.20	1:50

*Natural pH solutions

Three of the 11 natural pH leachates that were equilibrated under aerobic atmospheres (SRC liquefaction residue, water-quenched slag, and fly ash) were acidic (pH <6.2). Total mortality occurred during the screening procedures of these acidic leachates (table 22). These acidic leachates were relatively toxic (LC-50 <25.00 mL/100 mL) and at least a 1:10 dilution was necessary to ensure survival during a bioassay (tables 24 and 25).

Many factors probably contributed to the acute toxicity of the acidic leachates. It has been demonstrated (Griffin et al., 1978) that total mortality occurs when fathead minnow fry are exposed to acidic reconstituted water (pH <5.9) for 96 hours. Since the test organisms were propagated and held in water having a pH of approximately 7.4 and then experienced a rapid change in pH, the mortality was partially due to "ionic shock." A rapid lowering of the pH disrupts the Na^+/H^+ exchange system of fish and results in a loss of sodium that can cause death (Giles and Vanstone, 1976). Some of the acidic leachates also contained concentrations of Al, Cr, Cu, Mg, Ni, and Zn, which under laboratory conditions have been shown to be acutely toxic to fish (Brown, 1968; Doudoroff and Katz, 1953; Eaton, 1973; McCarty, Henry, and Houston, 1978; Pickering, 1974; and Pickering and Gast, 1972).

The natural pH leachates generated from the H-Coal liquefaction residue and the low-sulfur gob were relatively alkaline (pH >8.3) and acutely toxic during the screening procedure (table 22). The organisms were propagated and held in water having a pH of approximately 7.4; they experienced a rapid change in pH during the bioassays. Thus the mortality might partially be caused by the rapid rise in pH, since 5 percent and 50 percent mortality occurred in bioassays of reconstituted water with pH's of 9.2 and 10.0, respectively. The short-term acute toxicity of three of these four natural pH leachates, however, was eliminated with little dilution (<1:1.5), and HC-5 required a 1:6 dilution to ensure survival during a 96-hour bioassay.

Because of the complex chemical composition of the leachates and the unknown synergistic and antagonistic effects of the chemical constituents composing the leachates, it is not possible from these experiments to determine specifically which chemical constituents were directly responsible for the observed mortality. This point is illustrated dramatically by the anaerobic leachates generated from SRC liquefaction residue. The pH of the leachate during the screening procedure was 7.3, yet 40 percent mortality occurred. In addition, none of the chemical constituents were present in concentrations exceeding known acute LC-50 values.

To determine more precisely which chemical constituents are responsible for the toxicity of coal solid waste leachates, it is necessary to perform additional chemical and biological analyses. Such analyses would include the determination of organic compounds found in the wastes and leachates, as well as bioassays of particular chemical constituents and mixtures of chemical constituents found in those leachates generated from coal solid wastes, such as Al, Cd, Cu, Mg, and Ni.

When coal solid wastes are disposed of in landfills, it is important to investigate how the waste leachates interact with earth materials; the results of our investigation of soil-leachate interactions were discussed earlier in this report. Unfortunately, because of the small amount of leachate used in the attenuation study, we were not able to conduct bioassays of the filtrates; however, Al, Fe, K, Mg, and Zn were present in large enough concentrations to pose a hazard. For example, the filtrates produced from the acidified SRC leachate often contained zinc in amounts higher than 0.87 mg/L, which was the LC-50 value for zinc using fathead minnows in soft water, determined by Pickering and Henderson (1966).

Filtrates from the two chars, the low-sulfur gob, the SRC liquefaction residue, and the two Lurgi ashes tested often contained more than 5 mg/L of potassium. Although potassium is not acutely toxic to fathead minnows at this concentration, it is acutely toxic to other aquatic organisms such as freshwater mussels (Imlay, 1973). Even though several elements in the leachates are attenuated by the soil, some are not affected; they may even be eluted from the soil and could become a hazard to the aquatic environment. The soil characteristics of a proposed disposal site for coal solid wastes, therefore, and the location and access to nearby water resources should be studied before the site is chosen.

This limited biological analysis of the potential hazard of coal solid wastes consisted of acute static bioassays of the waste leachates using fathead minnow fry. It is considered very important to increase the scope of this investigation to assess the environmental impact of coal solid wastes. Several types of aquatic organisms should be tested in addition to fish, although recommended safe levels for selected test fish such as the fathead minnow, *Pimephales promelas*, quite often provide protection to other aquatic animals and plants (U.S. EPA, 1972).

Patrick, Cairns, and Scheier (1968) made a comparative study of the effects of 20 pollutants on fish, snails, and diatoms and found that no single kind of organism was most sensitive in all situations. A literature review by Braunstein, Copenhaver, and Pfuderer (1977) indicated that crustaceans (such as *Daphnia magna*) and phytoplankton may be appreciably more sensitive to trace elements than are insects and fish. Preliminary experiments with *Daphnia magna* demonstrate that this zooplankter is more sensitive to SRC liquefaction leachate than the fathead minnow fry. A complete environmental assessment of coal solid wastes should therefore include acute ecological bioassays utilizing fish, zooplankton, phytoplankton, and possibly a detritovore—suggestions that have also been made in a recent EPA publication (EPA, 1977).

Besides conducting acute bioassays with several types of organisms, representing all major trophic levels, it is also essential to conduct chronic bioassays to assess the chronic effects of coal solid wastes. Long-lived organisms such as fish might be harmed by long-term exposure (directly or through the organism's food supply) to chemical constituents leached from coal solid wastes. Reduced reproduction, malformation, disease, reduced growth, or generally decreased ability to compete with other organisms could result from long-term sublethal exposure to potentially hazardous chemical constituents found in coal solid wastes. It is important, therefore, to investigate the accumulation and concentration of potentially hazardous chemical constituents found in coal solid wastes by lower trophic levels, as well as to investigate the chronic toxicity of coal solid wastes to long-lived aquatic organisms.

Finally, a battery of health effects tests must be conducted on coal solid wastes and leachates. The EPA has recommended (for a level 1 assessment) that the wastes be tested for the presence of microbial mutagenicity, rodent acute toxicity, and cytotoxicity. The specific tests include the Ames Test, the Rabbit Alveolar Macrophage (RAM) assay, the Human Lung Fibroblast (WI-38) Assays, and acute toxicity bioassays with rats. The tests detect a broad spectrum of potential health effects, are not as costly as long-term animal bioassays, and are relatively reliable (Smith, 1978). With these tests it is possible to screen wastes, including coal solid wastes and their leachates, for potential carcinogenicity, cytotoxicity, and other detrimental health effects.

SECTION 10

POTENTIAL POLLUTION HAZARD FROM COAL SOLID WASTES

Evaluating the potential pollution hazard of coal solid wastes involves comparing the quantities of the wastes and their constituents with standards for acceptable levels of these constituents in the environment. Unfortunately, no established standards exist that delineate which specific chemical or mineralogical compositions of coal solid wastes pose potential hazards. Similarly, no established standards exist that specify which concentrations of chemical constituents in aqueous effluents from coal solid wastes will cause significant environmental damage. This section addresses this problem by comparing the chemical analyses of the solid wastes and leachates and the bioassay data, with the Multimedia Environmental Goals (MEGs) (Cleland and Kingsbury, 1977) and the toxicant extraction procedure criteria (U.S. EPA, 1978) for hazardous wastes. Both MEGs and the toxicant extraction procedure were sponsored or proposed by the U.S. EPA.

MATE VALUES FOR SOLID WASTES

The effluent guidelines proposed in the MEGs are known as Maximum Acute Toxicity Effluents (MATE). A MATE value is a theoretical value calculated to predict the maximum concentration of a constituent that will not have adverse health or ecological effects after short-term exposure. MATE is now a defunct term that will be replaced by DMEG (Discharge MEG) in future publications (D. Kingsbury, 1980, personal communication). MATE_{LE1} values were calculated using equation 52 of MEGs Volume 1 (Cleland and Kingsbury, 1977, p. 112). They were based on ecological effects using the LC-50 data from Section 9 of this report.

Table 28 lists the MATE values for 50 inorganic constituents of solid wastes disposed of on land. Each constituent has two values: one based on predicted adverse effects to health, the other based on predicted adverse effects to soil ecosystems. The table also lists the concentrations of those constituents that were found to exceed their respective MATE values. Also listed are the MATE_{LE1} values, representing the MATE values measured for the solid wastes as a whole.

The MATE_{LE1} values indicated that eight of the 11 wastes were not acutely toxic. The remaining three had MATE_{LE1} values that indicated relatively low toxicity. On the other hand, the MATE values for the individual chemical constituents of the waste indicated that 20 of the 50 constitutents were present in greater concentrations than their MATE values. This implies that these 20 elements are potential pollution hazards—a statistic that does not agree well

TABLE 28. CONSTITUENTS IN COAL UTILIZATION SOLID WASTES EXCEEDING HEALTH- OR ECOLOGY-BASED MATE VALUES FOR INDIVIDUAL PARAMETERS AND $MATE_{LE1}$ VALUES FOR LAND DISPOSAL ACTUALLY DETERMINED FOR THE SOLID WASTE

	MATE*												
Parameter	Health (mg/kg)	Ecology (mg/kg)	Lurgi Ill. No. 5	Lurgi Ill. No. 6	Lurgi Rosebud	H-Coal	SRC	Fly ash	Bottom ash (slag)	High-temp. char	Medium-temp. char	High-S refuse	Low-S refuse
Ag	50	10											
Al	16,000	200	95,506	108,121	101,188	17,253	67,529	73,600	84,571	17,147	13,601	56,522	97,008
Au	N	N											
As	50	10	11		22		74	46				13	68
B	9,300	5,000											
Ba	1,000	500	760	950	3,900				500				
Be	6	11	15	12			11	16					
Br	N	N											
Ca	48,000	3,200	22,571	16,652	60,106	7,862	7,933	26,100	43,668	4,574	6,075	28,159	21,227
Cd	10	0.2	1.6	1.6	1.6	0.4	1.3	1.9	2	0.5	0.4	1.4	1.8
Ce	250,000	N											
Cl	260,000	N											
Cr	50	50	171	212	55		100	130	100				78
Co	150	50											
Cu	1,000	10	50	57	49	14	100	140	40	14	11	29	36
F	7,500	N											
Fe	300	50	151,016	143,780	60,059	23,662	135,169	134,400	137,267	23,951	5,860	86,157	24,813
Ga	15,000	N											
Ge	1,700	N											
Hf	150	N											
Hg	2	50											
K	N	4,600	12,867	14,611	5,230		8,717	20,900	13,365			9,962	17,102
La	340,000	N											
Li	70	75											
Mg	18,000	17,000			21,531								
Mn	50	20	2,014	1,859	929	77	155	380	465	77	57	310	310
Mo	15,000	1,400											
Na	160,000	N											
Ni	45	2	195	89	5	21	14	160	57	20	12	48	55
Pb	50	10	182	45	38	32	59	110	20	12		55	55

TABLE 28. *Continued.*

Parameter	MATE* Health (mg/kg)	MATE* Ecology (mg/kg)	Lurgi Ill. No. 5	Lurgi Ill. No. 6	Lurgi Rosebud	H-Coal	SRC	Fly ash	Bottom ash (slag)	High-temp. char	Medium-temp. char	High-S refuse	Low-S refuse
P	3,000	0.1	218	87	2,095	44	1,004	873	786	87	87	829	1,397
Rb	360,000	N											
S_{Total}	N	N											
Sb	1,500	40											
Sc	160,000	N											
Se	10	5						16					
Si	30,000	N	245,653	229,946	225,739	39,641	110,930	194,300	222,934	40,015	50,490	145,490	261,380
Sm	160,000	N											
Sn	N	N											
Sr	9,200	N											
Ta	15,000	N											
Te	300	N											
Th	130	N											
Ti	18,000	160	6,415	6,295	6,475	1,019	1,7[illegible]	5,100	4,436	959	4,318	4,668	8,298
Tl	300	N											
U	12,000	100											
V	500	30	172	184	30.8	33	112	230	56			35.3	39.8
W	3,000	N											
Zn	5,000	20	1,500	400	31	71		560	62	48	42	300	500
Zr	1,500	N											

$MATE_{LE1}$ values† measured for solid waste (mg waste/kg soil) are as follows: Lurgi No. 5: >2 x 10^6 (nontoxic); Lurgi No. 6: >2 x 10^6 (nontoxic); Lurgi Rosebud: >2 x 10^6 (nontoxic); H-Coal: >2 x 10^6 (nontoxic); SRC: 42,000; fly ash: 18,000; bottom ash: 45,000; high-temp. char: >2 x 10^6 (nontoxic); medium-temp. char: >2 x 10^6 (nontoxic); high-S refuse: >2 x 10^6 (nontoxic); low-S refuse: >2 x 10^6 (nontoxic).

N = none.

*From Appendix C of Cleland and Kingsbury, 1977; values listed here are 100 times those listed in Appendix C to reflect January 1978 model changes.

†$MATE_{LE1}$ (μg/g) = 0.002 x $MATE_{WE}$ (μg/L); $MATE_{WE}$ (μg/L) = 100 x LC_{50}(mg/L).

TABLE 29. DISCHARGE SEVERITIES FOR CONSTITUENTS IN COAL UTILIZATION SOLID WASTES EXCEEDING HEALTH- OR ECOLOGY-BASED SOLID WASTE MATE VALUES

Parameter	MATE Health (mg/kg)	MATE Ecology (mg/kg)	Lurgi No. 5	Lurgi No. 6	Lurgi Rosebud	H-Coal	SRC	Fly ash	Bottom ash (slag)	High-temp. char	Medium-temp. char	High-S refuse	Low-S refuse
Ag	50	10											
Al	16,000	200	478	541	506	86	338	368	423	86	68	283	485
Au	N	N											
As	50	10	1		2		7	5				1	7
B	9,300	5,000											
Ba	1,000	500	2	2	8				1				
Be	6	11	2	2			2	3					
Br	N	N											
Ca	48,000	3,200	7	5	19	2	2	8	14	1	2	9	7
Cd	10	0.2	8	8	8	2	6	9	10	2	2	7	9
Ce	250,000	N											
Cl	260,000	N											
Cr	50	50	3	4	1		2	3	2				2
Co	150	50											
Cu	1,000	10	5	6	5	1	10	14	4	1	1	3	4
F	7,500	N											
Fe	300	50	3,020	2,876	1,201	473	2,703	2,688	2,745	479	117	1,723	496
Ga	15,000	N											
Ge	1,700	N											
Hf	150	N											
Hg	2	50											
K	N	4,600	3	3	1		2	5	3			2	4
La	340,000	N											
Li	70	75											
Mg	18,000	17,000			1								
Mn	50	20	101	93	46	4	8	19	23	4	3	15	15
Mo	15,000	1,400											
Na	160,000	N											
Ni	45	2	97	44	2	10	7	80	28	10	6	24	27
Pb	50	10	18	4	4	3	6	11	2	1		5	5
P	3,000	0.1	2,180	870	20,950	440	10,040	8,730	7,860	870	870	8,290	13,970
Rb	360,000	N											
S_{Total}	N	N											
Sb	1,500	40											
Sc	160,000	N											
Se	10	5						3					
Si	30,000	N	8	8	8	1	4	6	7	1	2	5	9
Sm	160,000	N											
Sn	N	N											
Sr	9,200	N											
Ta	15,000	N											
Te	300	N											
Th	130	N											
Ti	18,000	160	40	39	40	6	11	32	28	6	27	29	52
Tl	300	N											
U	12,000	100											
V	500	30	6	6	1	1	4	8	2			1	1
W	3,000	N											
Zn	5,000	20	75	20	2	4		28	3	2	2	15	25
Zr	1,500	N											
Total discharge severity			6,054	4,531	22,805	1,033	13,152	12,020	11,155	1,463	1,100	10,412	15,118

Discharge severity = concentration/MATE

with the results generated by the $MATE_{LE1}$ values for the wastes (that eight were not acutely toxic). It seems, therefore, that the MATE values for solid waste disposal on land are perhaps conservative when applied to coal solid wastes.

The discrepancy between the estimated hazard based on MATE values for individual chemical constituents and the measured toxicity of the leachates seems to originate in the assumption (during the derivation of the MATE value) that the solid waste is highly soluble in water. Coal solid wastes are generally made up of materials of relatively low water solubility; this contradicts the assumption and may be the reason for the overestimation of the hazard for these particular wastes.

Another method to further evaluate the toxicity of the constituents is comparing their discharge severities (concentration/MATE value). After doing so (table 29), it is clear that Al, Fe, and P are predicted to have the most potential for exceeding discharge limits and posing environmental problems.

MATE VALUES FOR LEACHATES

The MATE values for water quality of the chemical constituents measured in the leachates from the coal wastes are given in tables 30 and 31. The tables also provide a listing of those constituents in the leachates that exceeded their MATE values for individual parameters (appendix C in Cleland and Kingsbury, 1977), along with a listing of $MATE_{WE}$ values (Cleland and Kingsbury, 1977, eq. 50, p. 111), which are based on ecological effects and acute bioassay data that were obtained using the leachates from the wastes (Section 9).

TABLE 30. $MATE_{WE}$ VALUES MEASURED FOR LEACHATES, BASED ON ECOLOGICAL EFFECTS AND BIOASSAY DATA

Leachate	$MATE_{WE}$ value* (μg/L)	LC_{50} 96-hr (ppm)	Mortality, full strength leachate (%)	Dilution for no mortality†
Lurgi No. 5	$>10^9$	$>10^7$	0	None
Lurgi No. 6	$>10^9$	$>10^7$	0	None
Lurgi Rosebud	$>10^9$	$>10^7$	0	None
H-Coal	$>10^9$	$>10^7$	15	1:1
SRC	2.1×10^7	210,000	100	1:10
Fly ash	9×10^6	90,000	100	1:100
Bottom ash (slag)	2.25×10^7	225,000	100	1:28
High-temp. char	$>10^9$	$>10^7$	0	None
Medium-temp. char	$>10^9$	$>10^7$	5	1:1
High-S refuse	$>10^9$	$>10^7$	5	1:1
Low-S refuse	$>10^9$	$>10^7$	15	1:1

*$MATE_{WE}$ (μg/L) = 100 x LC_{50}(mg/L)

†No mortality during 96-hour bioassay.

TABLE 31. CONSTITUENTS IN LEACHATES EXCEEDING HEALTH- OR ECOLOGY-BASED WATER MATE VALUES FOR INDIVIDUAL PARAMETERS

	MATE*												
Parameter	Health (mg/L)	Ecology (mg/L)	Lurgi Ill. No. 5	Lurgi Ill. No. 6	Lurgi Rosebud	H-Coal	SRC	Fly ash	Bottom ash (slag)	High-temp. char	Medium-temp. char	High-S refuse	Low-S refuse
Al	80	1				3.0		62.6	5.5				
As	0.25	0.05											
B	47	25			26.9			58					
Ba	5	2.5											
Be	0.03	0.055											
Ca	240	16	470	290	210	110	415	508	17.5	93	207	480	568
Cd	0.05	0.001		0.02	0.02			0.39					
Cl	1,300	N											
Cr	0.25	0.25											
Co	0.75	0.25						0.31					
Cu	5.0	0.05						0.20	0.20				
F	7.0	N			8.0								
Fe	1.5	0.25					1.0	13.5	0.60				1.08
Hg	0.25	0.22											
K	N	23	30	42									
Li	0.33	0.38	1.00	1.8				0.53					
Mg	90	87											
Mn	0.25	0.10		0.45			0.93	9.14	0.78	0.28	0.57	1.83	0.59
Mo	75	7											
Na	800	N											
NH_4^+	N	N											
Ni	0.23	0.01	0.03	0.03				1.31	0.13				
Pb	0.25	0.05	0.1	0.1				0.15				0.20	0.15
P	15	0.0005											0.04
S^{-2}	N	N											
SO_4	1,250	N						2,350				1,600	
Sb	7.5	0.2			0.4								
Se	0.05	0.25											
Si	150	N											
Sn	N	N											
Sr	46	N											
Te	1.5	N											
Ti	90	0.82											
Tl	1.5	N											
V	2.5	0.15											
Zn	25	0.1		0.12				20	0.18				

*From Appendix C (Cleland and Kingsbury, 1977).

The MATE_{WE} values, which are the measured values of the leachates, were computed from the LC-50 values for the aerobic natural pH leachates, (see Section 9, this report). Eight of the 11 leachates produced a low mortality percentage (≤15 percent), whereas three of the leachates were highly toxic. The toxicity of the leachates from the fly ash and bottom ash was mainly caused by their acidity.

Comparing the MATE_{WE} values of the leachates to the table of constituents exceeding individual MATE values and to the discharge severities (table 32),

TABLE 32. DISCHARGE SEVERITIES FOR CONSTITUENTS IN LEACHATES FROM COAL SOLID WASTES EXCEEDING HEALTH- OR ECOLOGY-BASED WATER MATE VALUES

	MATE												
Parameter	Health (mg/L)	Ecology (mg/L)	Lurgi No. 5	Lurgi No. 6	Lurgi Rosebud	H-Coal	SRC	Fly ash	Bottom ash (slag)	High-temp. char	Medium-temp. char	High-S refuse	Low-S refuse
Al	80	1				3		63	5				
As	0.25	0.05											
B	47	25			1			2					
Ba	5	2.5											
Be	0.03	0.055											
Ca	240	16	29	18	13	7	26	32	1	6	13	30	35
Cd	.05	.001		20	20			390					
Cl	1,300	N											
Cr	0.25	0.25											
Co	0.75	0.25						1					
Cu	5.0	0.05						4	4				
F	7.0	N			1								
Fe	1.5	0.25					4	54	2				4
Hg	0.25	0.22											
K	N	23	1	2									
Li	0.33	0.38	3	5				2					
Mg	90	87											
Mn	0.25	0.10		4			9	91	8	3	6	18	6
Mo	75	7											
Na	800	N											
NH_4^+	N	N											
Ni	0.23	0.01	3	3				131	13				
Pb	0.25	0.05	2	2				3				4	3
P	15	0.0005											
S^{-2}	N	N											
SO_4	1,250	N						2				1	
Sb	7.5	0.2			2								
Se	0.05	0.25											
Si	150	N											
Sn	N	N											
Sr	46	N											
Te	1.5	N											
Ti	90	0.82											
Tl	1.5	N											
V	2.5	0.15											
Zn	25	0.1		1				200	2				
Total discharge severity			38	55	37	10	39	975	35	9	19	53	48

TABLE 33. CONSTITUENTS IN LEACHATES FROM COAL UTILIZATION SOLID WASTES

Parameter	Maximum allowable leachate (mg/L)	Lurgi No. 5		Lurgi No. 6		Lurgi Rosebud		H-Coal	
		Nat. pH 8.25	Adj. pH 6.05	Nat. pH 7.55	Adj. pH 5.10	Nat. pH 8.44	Adj. pH 4.95	Nat. pH 8.83	Adj. pH 5.01
Primary drinking water									
Arsenic	0.5								
Barium	10.0								
Cadmium	0.1								
Chromium (VI)	0.5								
Fluoride	14.0								
Lead	0.5								
Mercury	0.02								
Nitrate	100.0								
Selenium	0.1								
Silver	0.5								
Secondary drinking water									
Chloride	2,500.0								
Copper	10.0								
Hydrogen sulfide	0.5								
Iron	3.0								14.0
Manganese	0.5		4.2		1.94		16.2		1.67
Sulfate	2,500.0								
Total dissolved solids	5,000.0								
Zinc	50.0								
pH (units)	5.5-9.5								
Irrigation water									
Aluminum	20.0								
Beryllium	0.5								
Boron	2.0	5.0	6.8	4.0	4.5	26.9	29.9	11.0	11.6
Cobalt	5.0								
Molybdenum	.05					0.4			
Nickel	2.0								

Nat. = Natural

Adj. = Adjusted

reveals that only Ca and Mn consistently exceed their MATE values for most of the wastes. Fly ash leachate contains the most constituents that exceed MATE values, 13, compared to only two each for the H-Coal and the two char leachates. The measured MATE_{WE} values for the leachates represent acute toxicity, whereas those elements exceeding listed MATE values represent potential chronic toxicity problems. More data need to be collected and evaluated in order to validate the proposed MATE values and the use of discharge severities and acute toxicity data as a basis for predicting long-term environmental effects.

Another basis for evaluating the potential hazard posed by coal solid wastes is to compare the concentrations of constituents in the leachates from this study with the proposed U.S. EPA hazardous waste criteria (U.S. EPA, 1978). Before evaluating results, however, the two extraction procedures must be compared.

EXCEEDING PROPOSED U.S. EPA TOXICANT EXTRACTION PROCEDURE STANDARDS

SRC		Fly ash	Bottom ash (slag)	High-temp. char		Medium-temp. char		High-sulfur refuse		Low-sulfur refuse	
Nat. pH	Adj. pH	Nat. pH	Nat. pH	Nat. pH	Adj. pH	Nat. pH	Adj. pH	Nat. pH	Adj. pH	Nat. pH	Adj. pH
6.35	4.69	4.08	3.81	8.05	4.33	7.19	3.81	7.45	3.43	7.79	3.50
		0.39									
	31.2	13.5			250.0		4.75				10.0
0.93	1.38	9.14			4.45	0.57	3.20	1.83	14.7	0.59	12.6
		4.08	3.81								
		62.6									
4.0	4.0	58.0		2.8	2.5	10.0	9.1				

The procedure proposed by the EPA calls for screening through a 3/8-inch sieve, which can be compared to the 45-mesh sieve that was used in this study. The solid is then shaken in a volume of water that is 16 times its weight; in this study, the volume of water is nine times the solid's weight. In the EPA procedure, the sample is adjusted to pH 5.0 ± .1 with acetic acid; in this study, the pH was adjusted with nitric acid to several values, many of which were close to 5.0. The EPA procedure calls for a 24-hour shaking period; this study used a 6-month equilibration.

Clearly, the intent and the methods used for the two extraction procedures were quite similar; however, they cannot be directly compared. The effects of using acetic acid compared to using nitric acid, the effects of the differences in equilibration times, and the consequences of differences in final volumes is difficult to assess. Nevertheless, the results obtained by the two methods should be similar. Table 33 presents a tabulation of constituents of the leachates from this study that exceeded the proposed U.S. EPA maximum allowable effluent levels for primary and secondary drinking water parameters and for irrigation water standards for short-term (less than 20 years) application.

These results indicate that only Cd in the fly ash leachate exceeds the primary leachate standard (10 times drinking water) and would thus be classed as a hazardous waste by the proposed U.S. EPA criteria. It is useful to compare the secondary drinking water parameters and note that Mn and Fe frequently exceed 10 times the drinking water standard level. This occurs mainly in the acidified leachates as compared to the natural pH leachates. When making these comparisons, the differences between our procedure and the EPA procedure should be kept in mind, particularly the two differences in final volume and in pH.

Interestingly, boron exceeds the irrigation water standard in the leachates from nearly all the coal wastes and at all pH levels. This is a potentially serious problem in the western states, where high levels of boron in irrigation waters are a problem because of the toxicity of boron to plants. This illustrates that the ecologically based MATE value for boron may need to be lowered to be more consistent with irrigation water standards.

Of the leachates obtained from the 11 coal solid wastes at their natural pH level, only the fly ash leachate contained a significant level of acute toxicity. Whereas the acute toxicity of most coal ash leachates was low, however, they were measured with only one species of organism, and the potential for long-term pollution that could cause chronic toxicities is unknown. The elements in the leachates that exceeded the MATE values for water quality and irrigation water standards may be a guide to potential long-term pollution problems.

The thermochemical modeling indicated several of the leachates were in a metastable equilibrium. For example, the pyrites and pyrrhotites in the coal-cleaning and liquefaction residues will eventually oxidize to form an acidic leachate, which would have a much higher acute toxicity than was measured at its natural pH in this study. The toxicity to be expected upon oxidation of the metastable minerals would be more closely estimated from the bioassay and chemical data from the acidified leachates. Thus, all these chemical, mineralogical, biological, and soil attenuation factors must be integrated when assessing the environmental impact of land disposal of the solid wastes from coal utilization processes.

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APPENDIX

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